

# Synchrotrons, X-rays, and Energy Related Research

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# Outline

- Introduction

- Synchrotron Radiation

- Experimental

- Photoemission & X-ray Absorption

- Ag Clusters

- Radiation Damage

- CdTe Solar Cells

- Acknowledgements

# COLLABORATORS

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- Students

- Nadia Leyarovska - Illinois Institute of Technology
- Xiangxin (Shine) Liu - University of Toledo
- Tessa Rivere - University of Missouri, Columbia

# Synchrotrons

RAL CAMPUS

CONFERENCE CENTER

RF / EXTRACTION BLDG.

BOOSTER /  
INJECTOR

LOW-ENERGY UNDULATOR  
TEST LINE

EXPERIMENT HALL

STORAGE RING

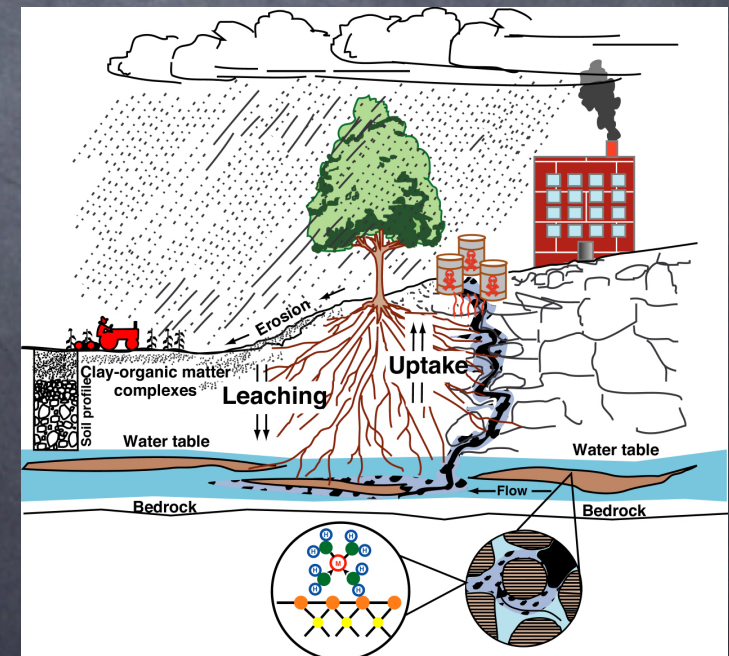
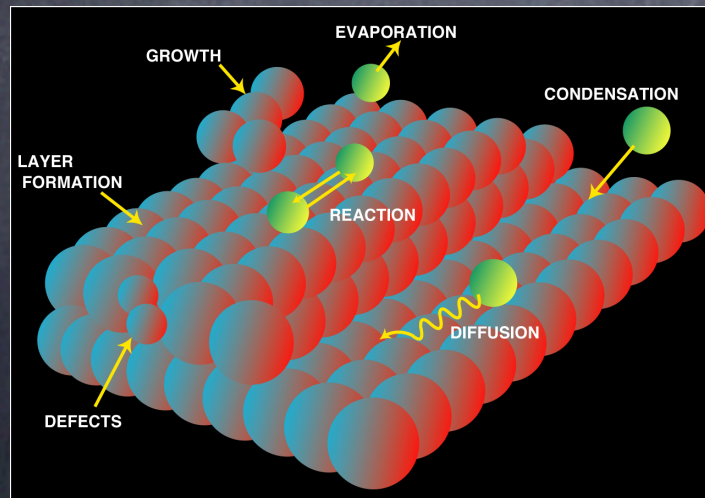
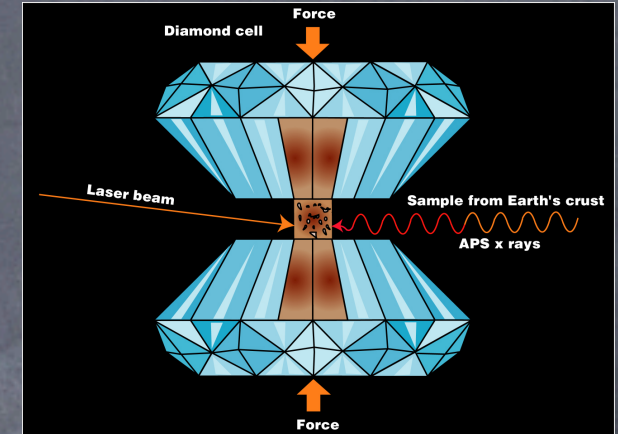
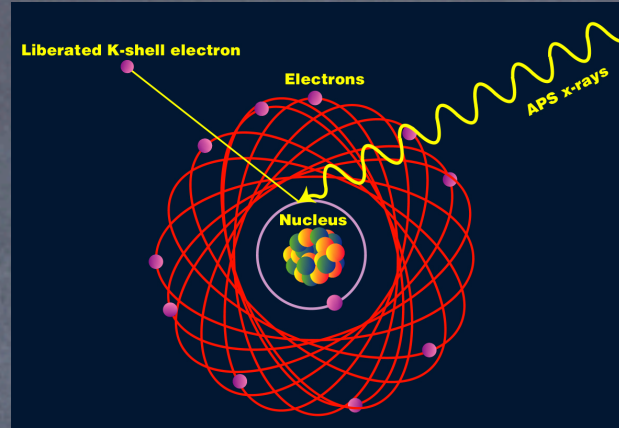
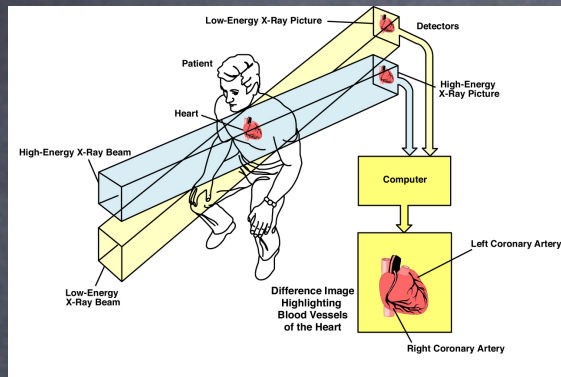
LINAC / INJECTION BLDG.

LAB/OFFICE MODULES

LAB/OFFICE MODULES



# Synchrotron Science



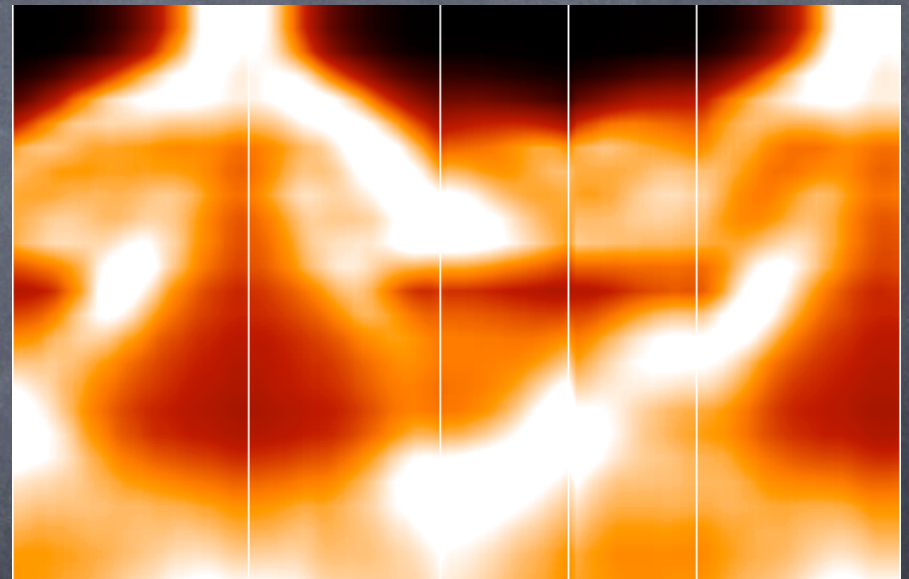
# Electronic Structure

## • Electron Dispersion

- Mechanical Stability
- Corrosion Resistance
- Chemical Reactivity
- Electrical Conductivity
- Thermal Conductivity
- Magnetism

• Wolfgang Eberhardt

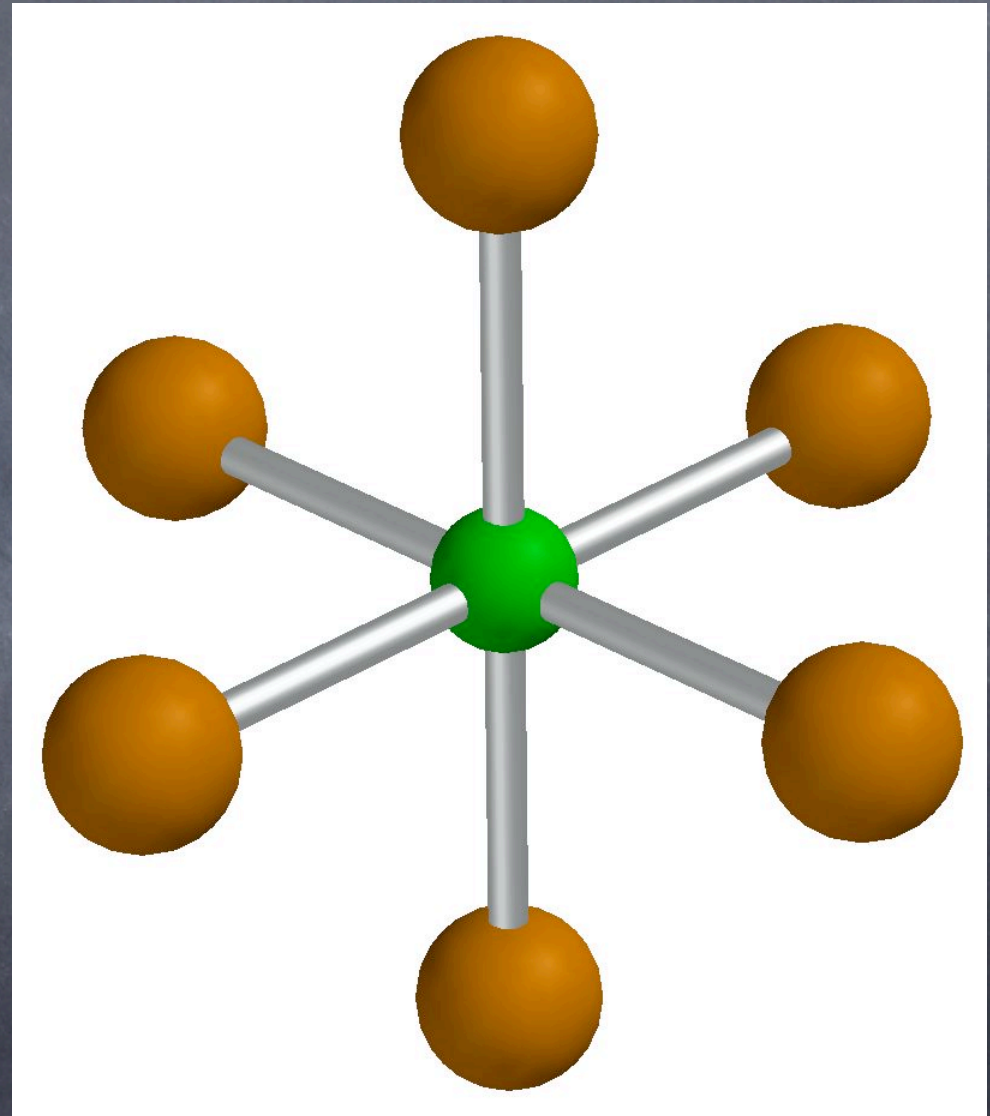
H-Si(111) 1x1



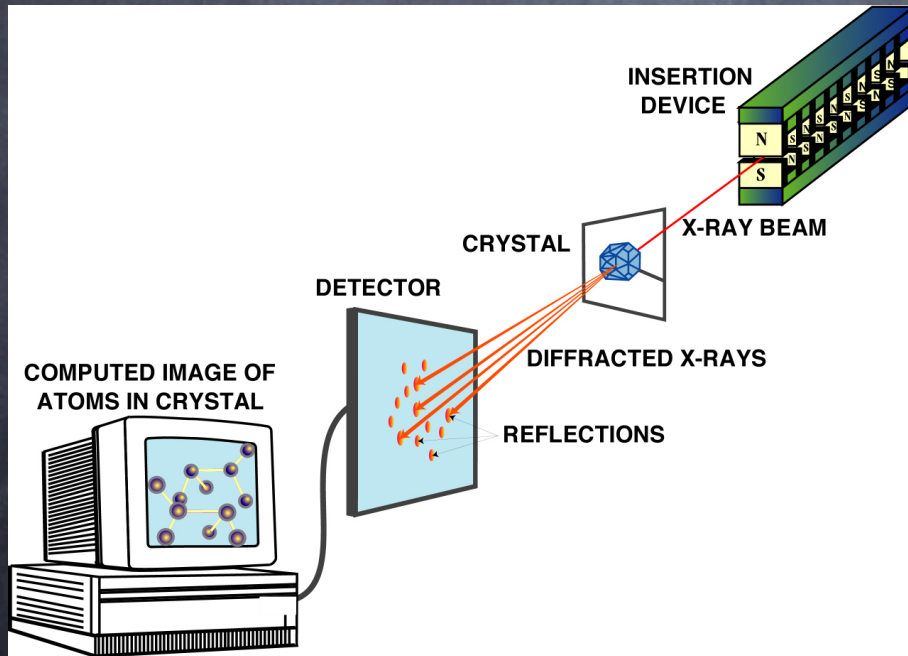
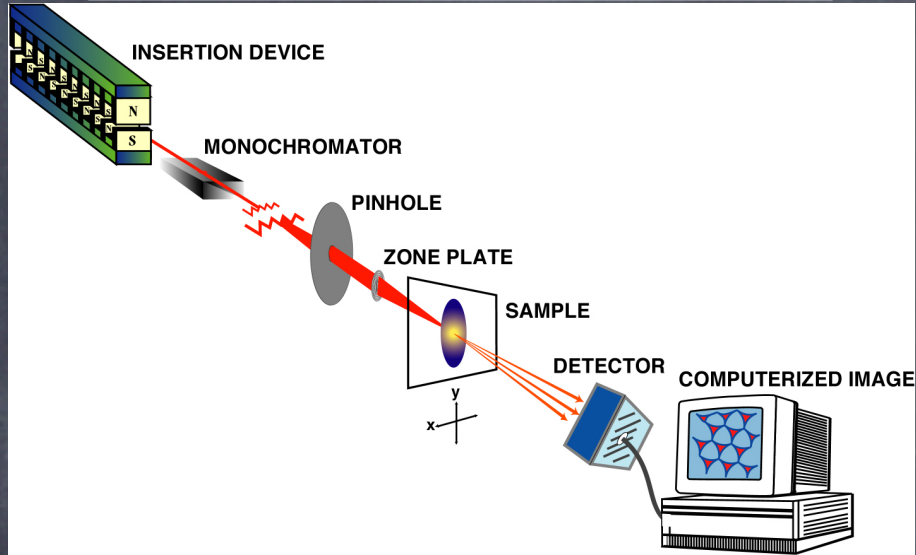
W       $\Gamma$       U      W      K       $\Gamma$

# Geometric Structure

- Atom Positions
- Atom Types
- Bond Lengths
- Geometry

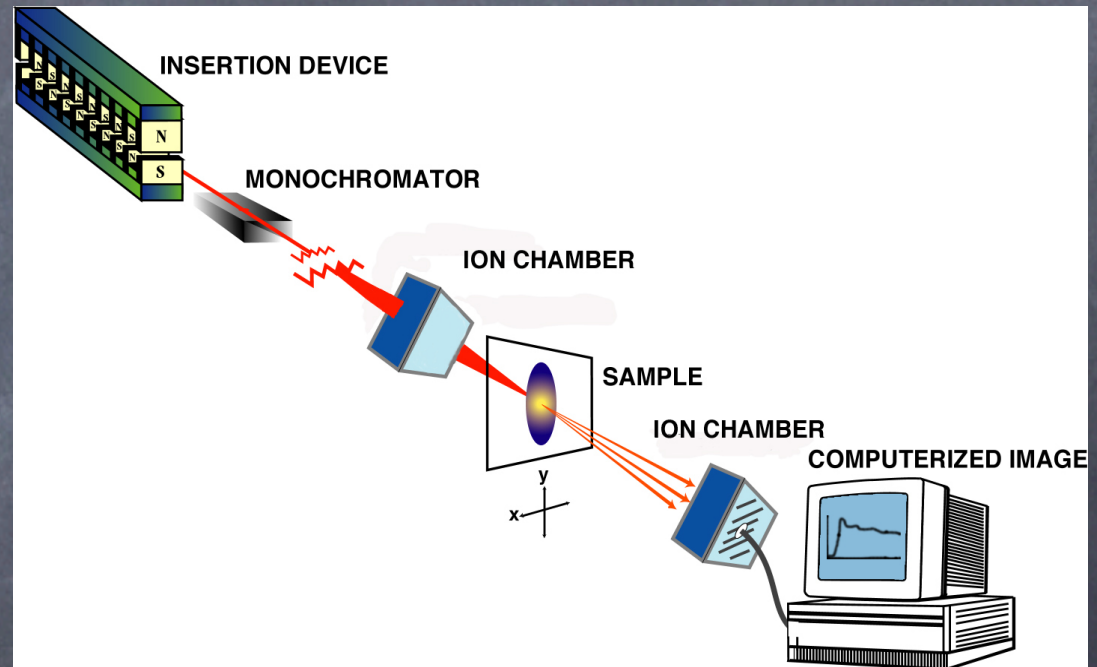


# X-ray Microfocus



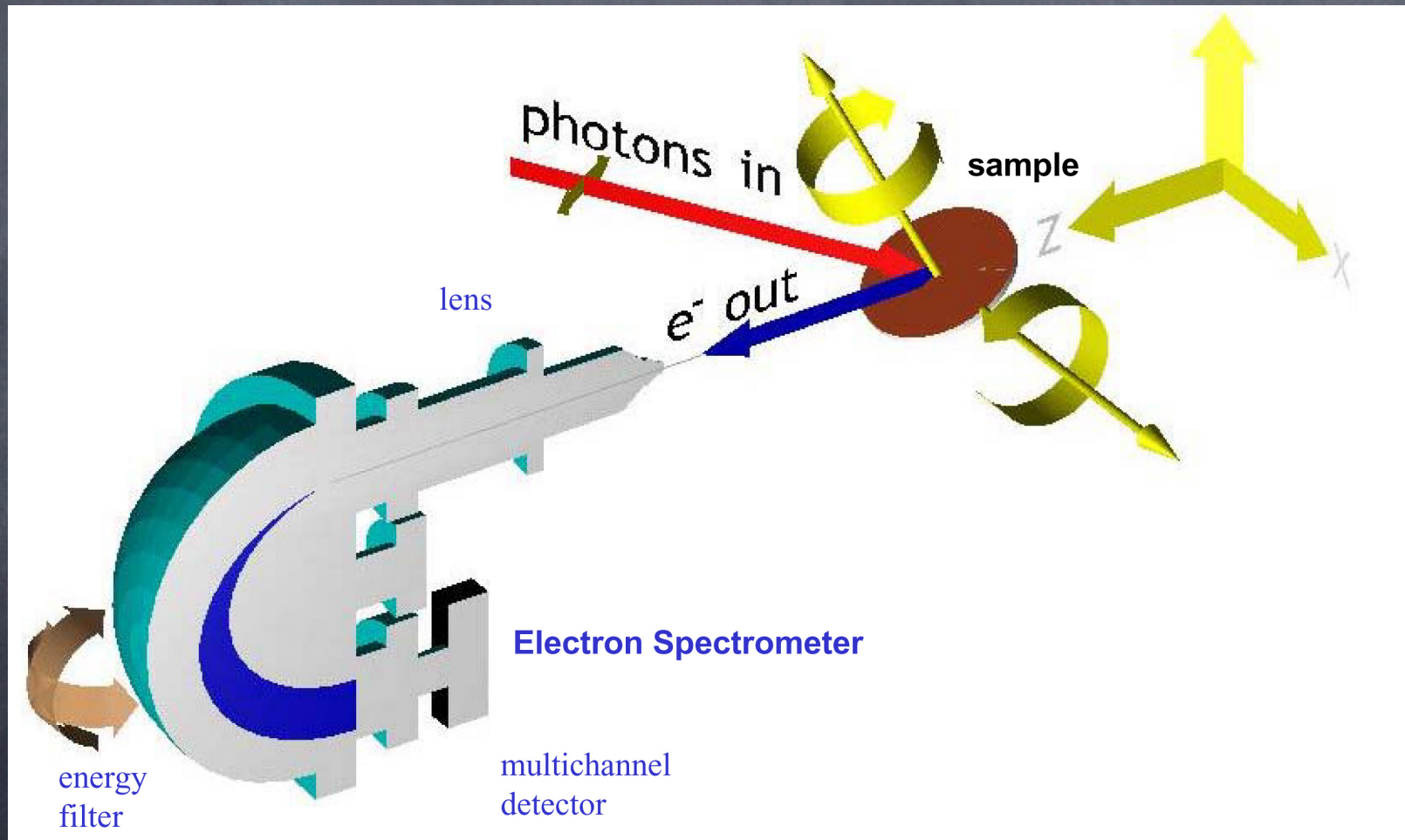
# X-ray Scattering

# MR-CAT Materials Research



# X-ray Absorption

# Photoemission Measurement



# X-ray Techniques

- Photoelectric Effect
  - Photon In
  - Electron Out
- Every Atom Has Orbitals With Different Binding Energies

# PHOTOEMISSION

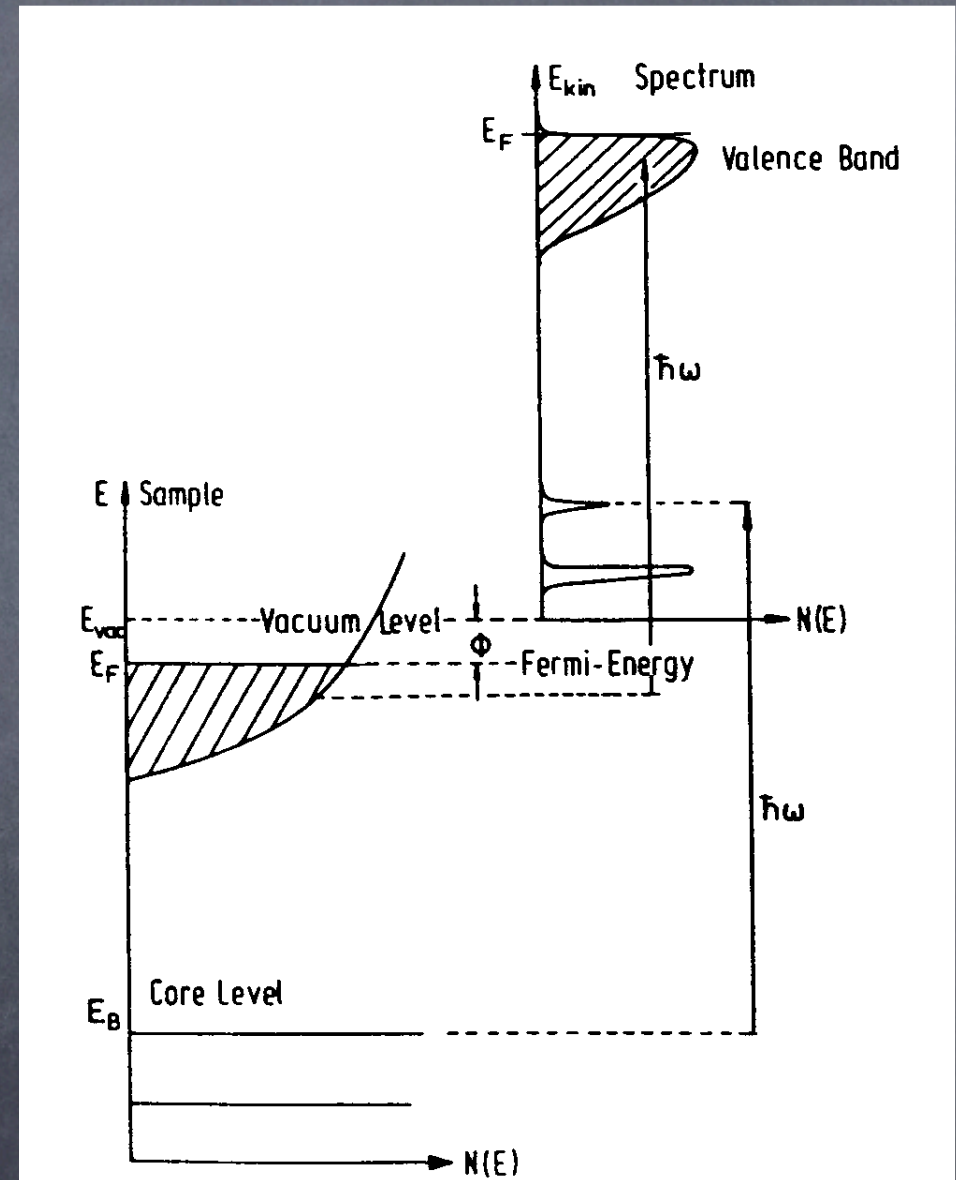
- Photoelectric Effect

- Photon In

- Electron Out

- $KE = h\nu - BE - \phi$

- Probes Occupied Electronic States



# Cross Section

- How do we understand photoemission?

$$\sigma_{nl}(E) = \frac{4}{3}\pi^2\alpha a_0^2 \left[ N_{nl}(E - E_{nl}) \frac{1}{2l+1} \right] \left[ l R_{E,l-1}^2 + (l+1) R_{E,l+1}^2 \right]$$

where  $\alpha$  is the fine structure constant;  $a_0$  is the Bohr Radius,  $N_{nl}$  is the number of electrons in the subshell,  $E_{nl}$  is the binding energy of the level, and  $E$  is the energy of the ejected electron.

$$R_{E,l\pm 1} = \int_0^\infty P_{nl}(r) r P_{E,l\pm 1}(r) dr$$

where  $P_{nl}(r)$  is the radial part of the wavefunction.

# Theory

- Three Step Model

- W. Spicer

- Photoexcitation

- Transition Matrix Element

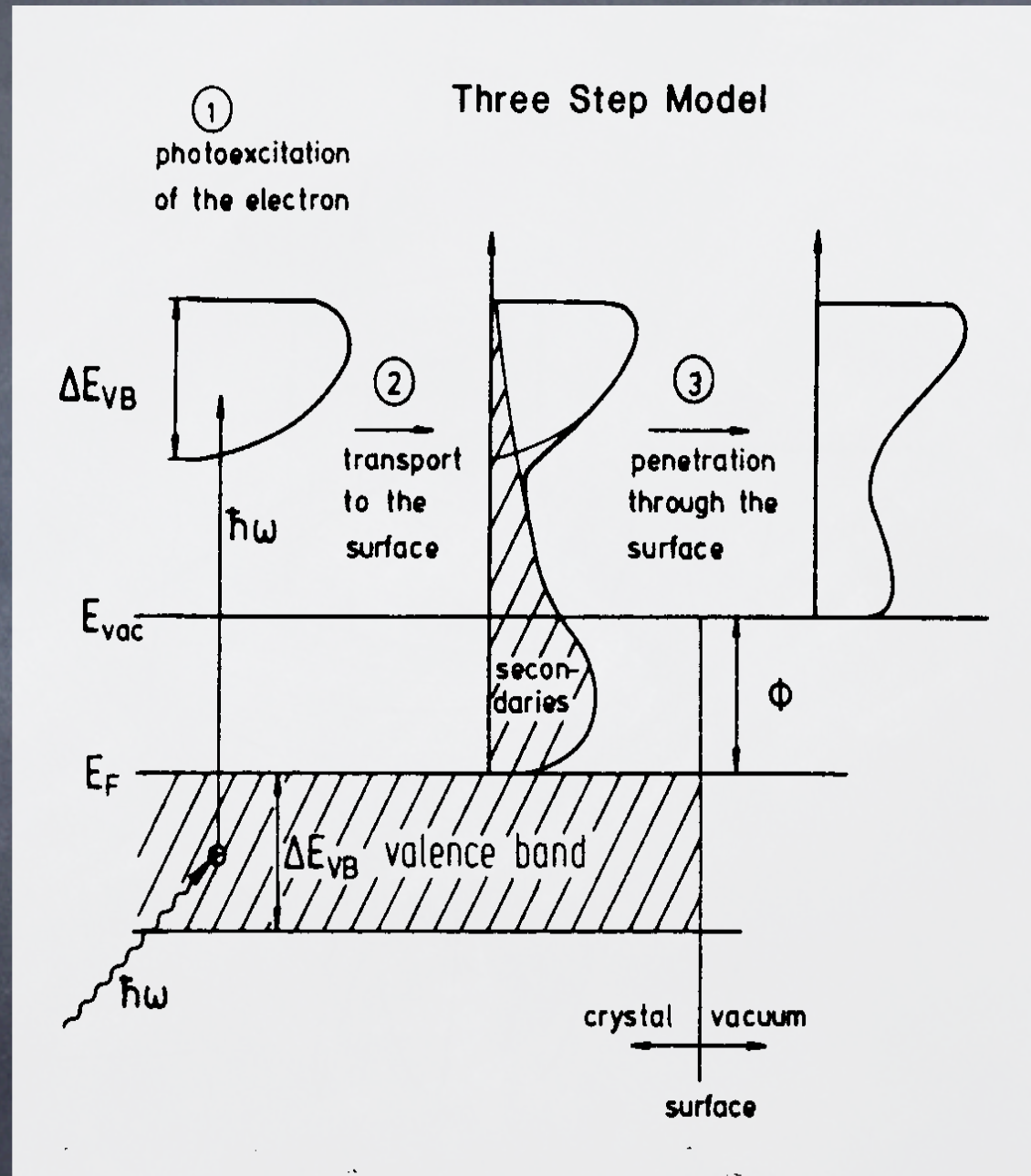
- Transport to Surface

- $KE > \text{Vacuum Level}$  but e-located inside crystal

- Scattering

- Escape from Surface

- Refraction at Barrier



# EXAFS Theory

## • Single Scattering Approximation

$$TP \propto \frac{2\pi}{\hbar} \left| \langle \psi_f | \varepsilon \cdot r | \psi_i \rangle \right|^2 \delta(E_F - E_i - \hbar\omega)$$

*but  $\psi_f$  is complicated.*

$$\psi_f = \psi_0 + \sum_j \psi_j$$

$$\psi_0 \sim \left( \frac{e^{ikr}}{kr} \right) \text{ and } \psi_j \sim \left( \frac{e^{ik|\vec{r} - \vec{r}_j|}}{k|\vec{r} - \vec{r}_j|} \right)$$

*Define a function,*

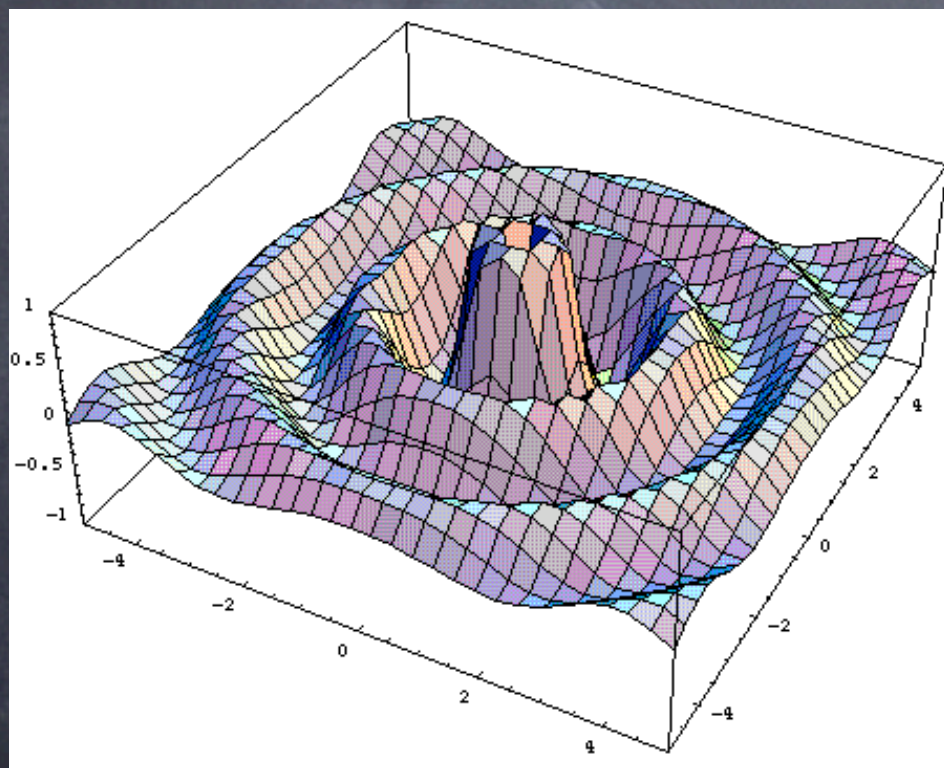
$$\chi = \sum_j \frac{\psi_0^* \psi_j + \psi_j^* \psi_0}{\psi_0^* \psi_0}$$

# EXAFS Equation

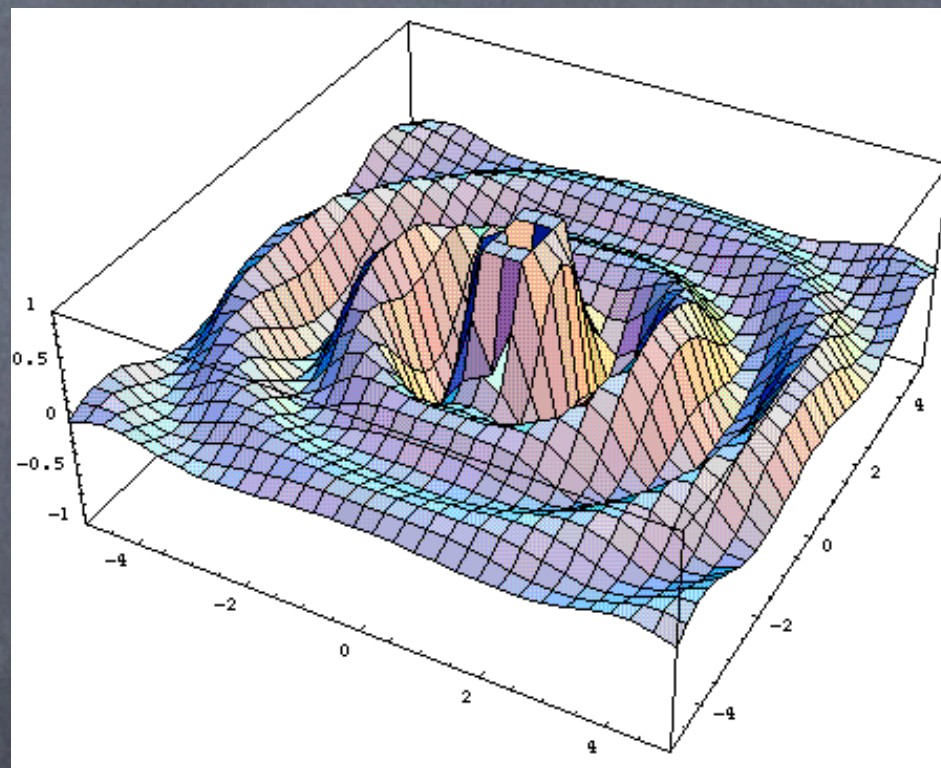
$$\chi(k) = \sum_j \frac{N_j f_j(k)}{r_j^2} e^{\frac{-2r_j}{\lambda(k)}} e^{-2k^2 \sigma_j^2} \sin(2kr_j + 2\delta_e + \delta_j)$$

# EXAFS

No Scatterers

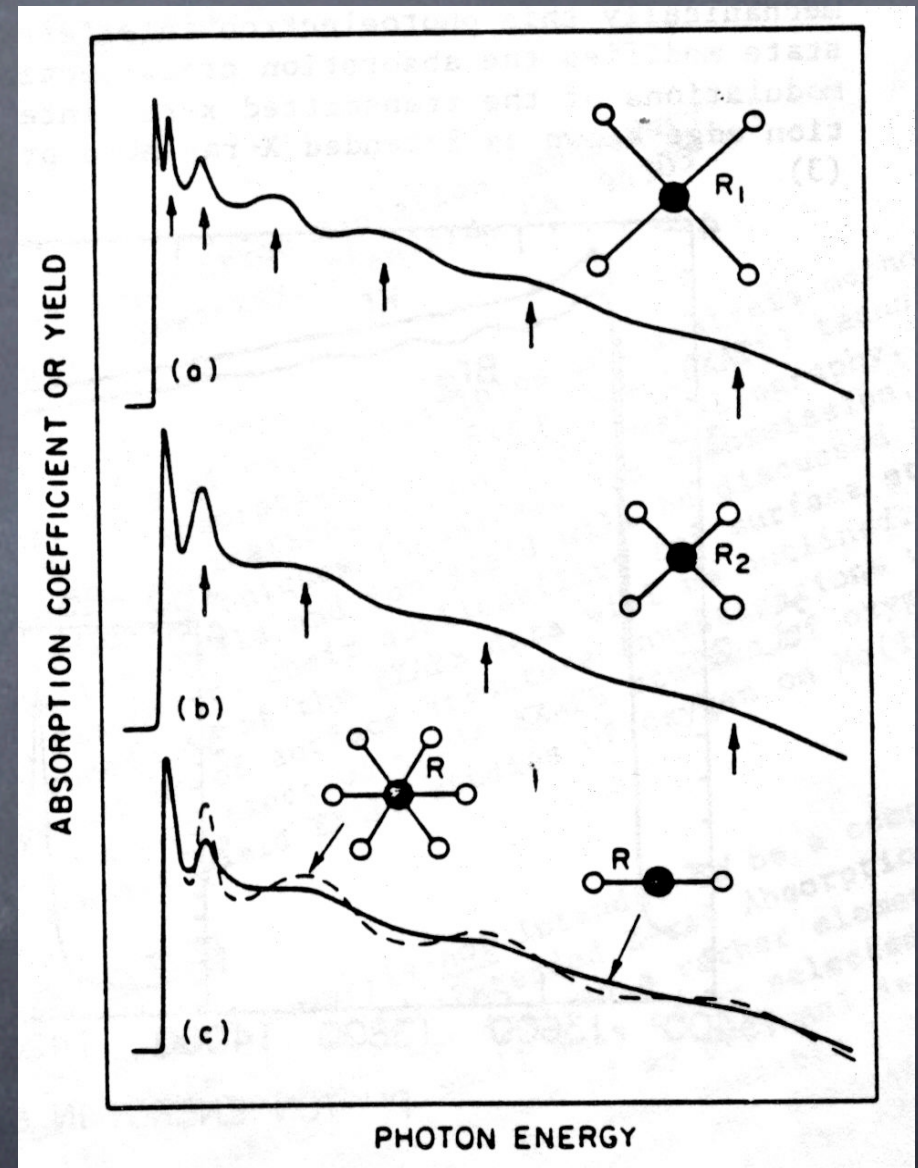


Scatterers



# Fine Structure

- Fine Structure
  - $R_1 > R_2$ 
    - Higher Frequency Oscillations
  - $N_1 > N_2$  at fixed  $R$ 
    - Higher Amplitude Oscillations
  - Same Frequency

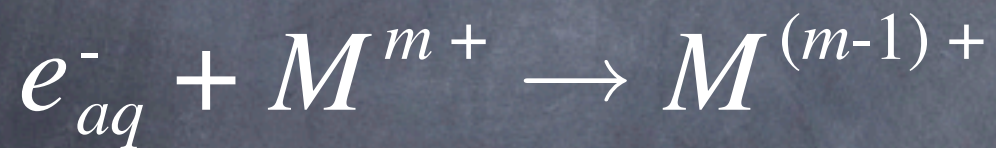
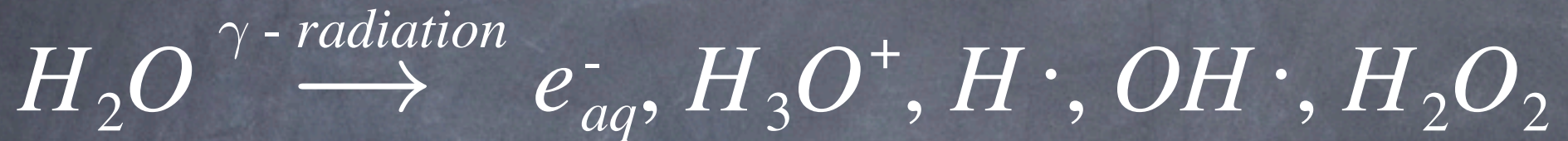


J. Stohr Nexafs Spectroscopy

# Ag/X Clusters X=Pt/Pd

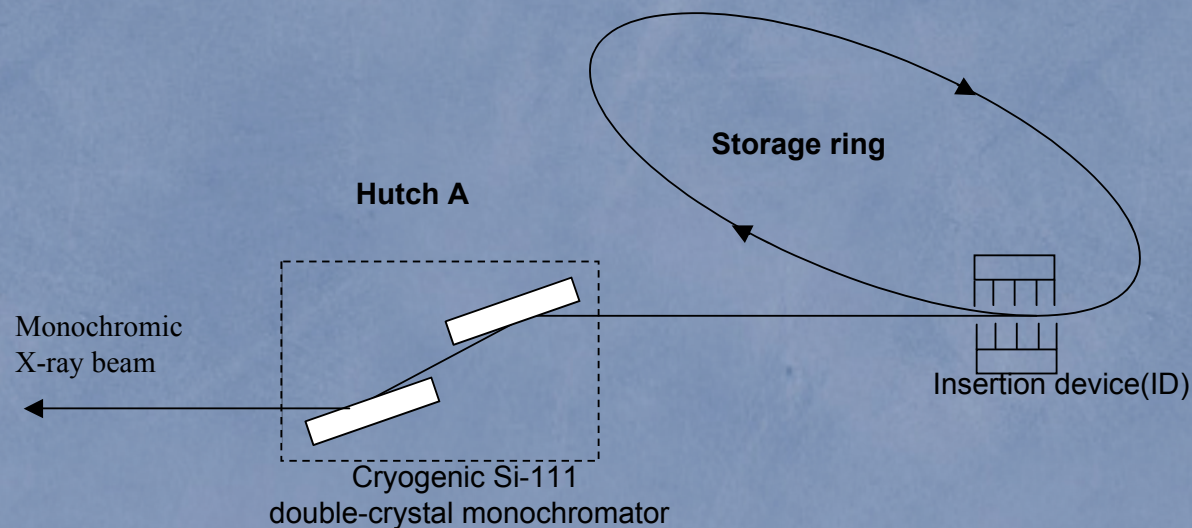
- Aqueous Metal Salt Solution
- Mole Ratios 20/80 to 80/20
- Radical Scavenger 2-propanol
- Poly(vinyl alcohol)
- Gamma Irradiation at UMR Reactor Pool
  - 36-48 Hours 3-3.5kGy
- Radiolysis

# Radiolysis

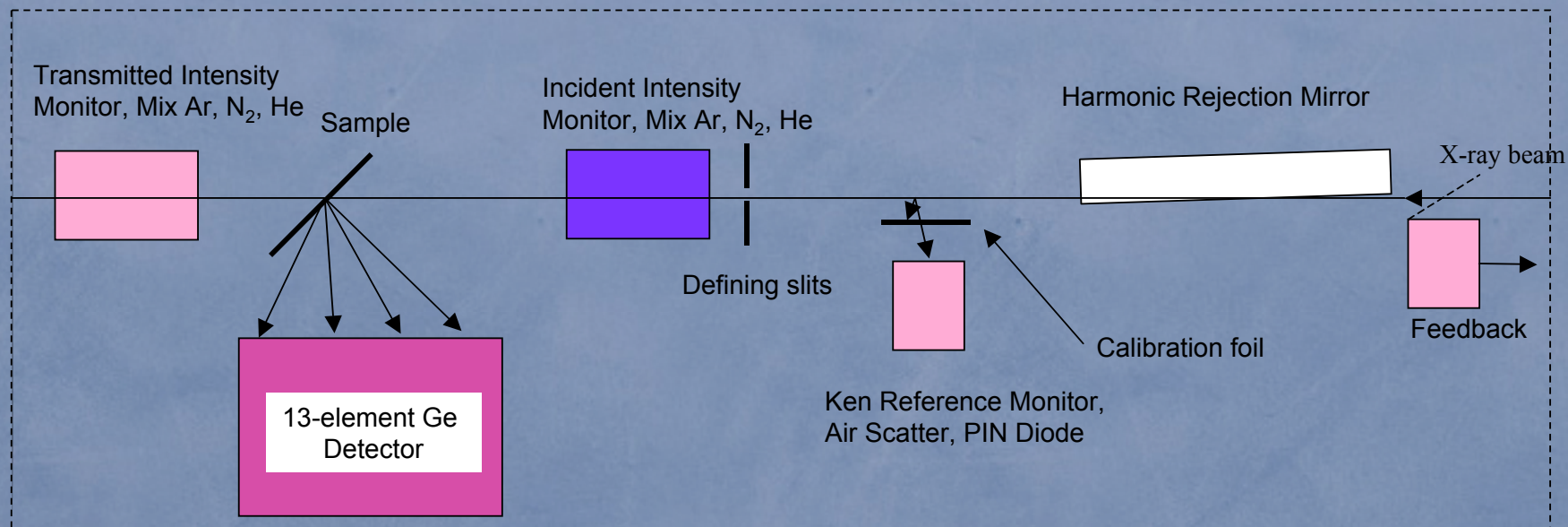


# XAS Experimental

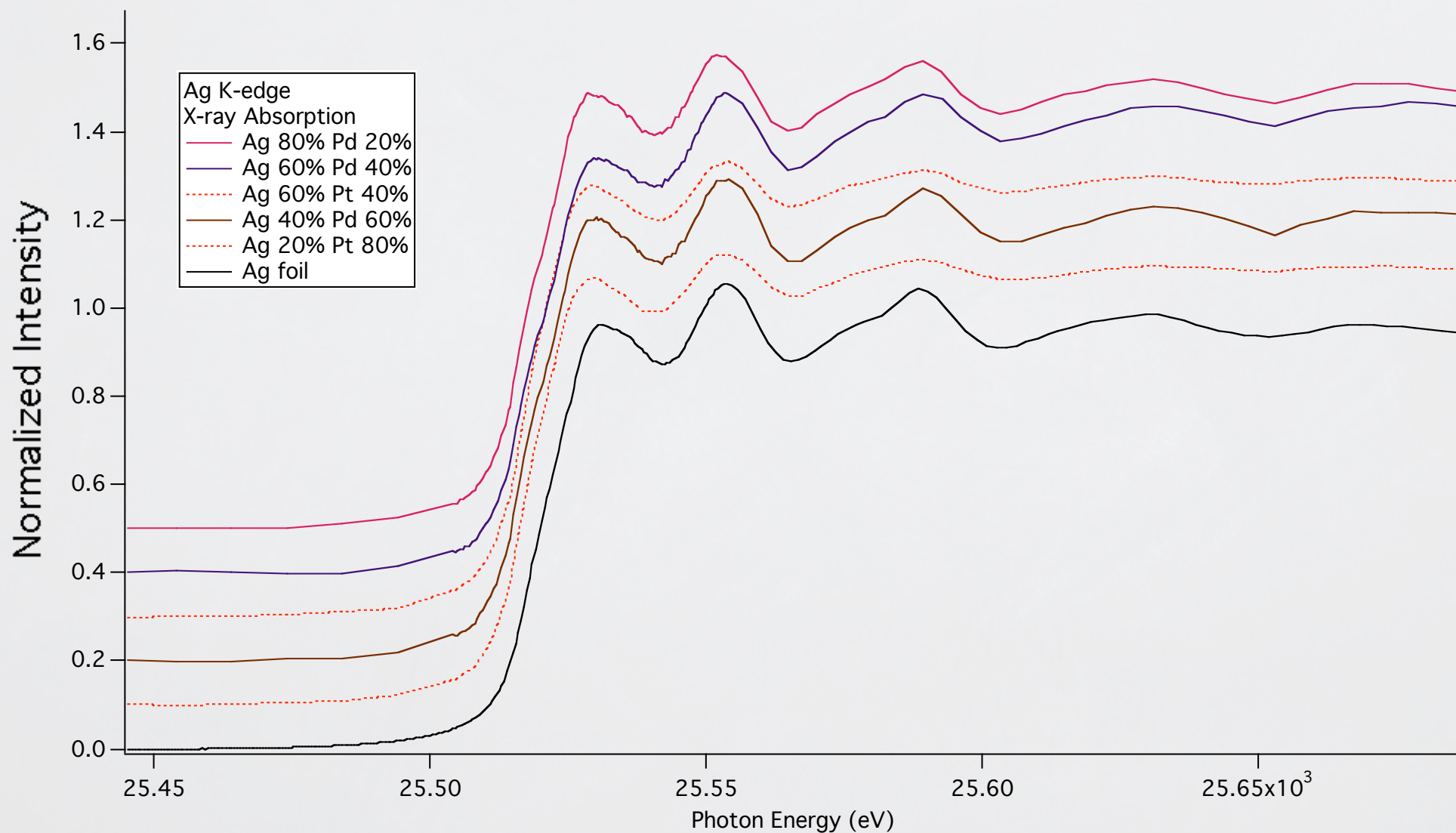
## MRCAT Beamline, Sector 10ID-B, Advanced Photon Source



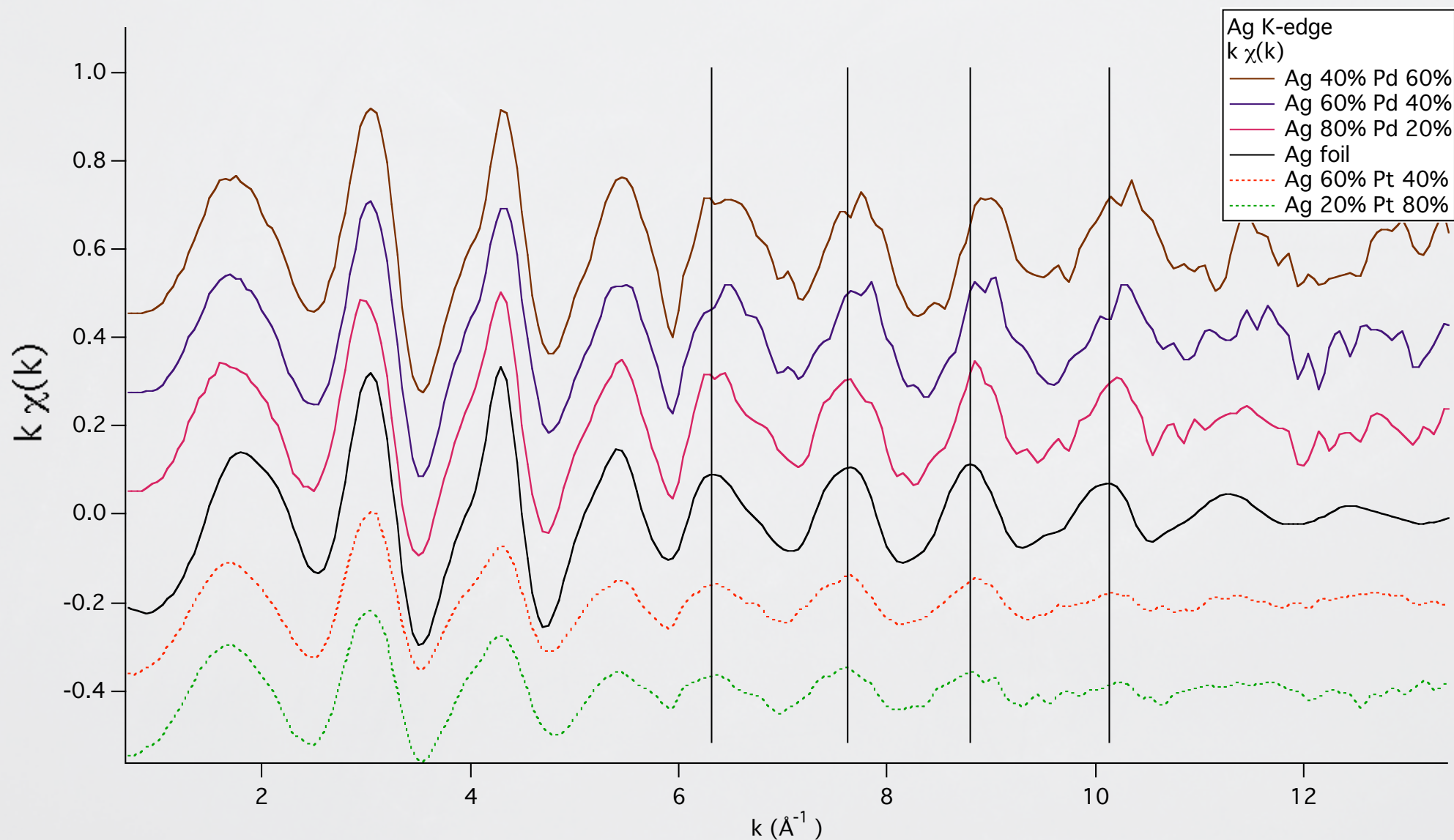
### **Experimental Hutch B**



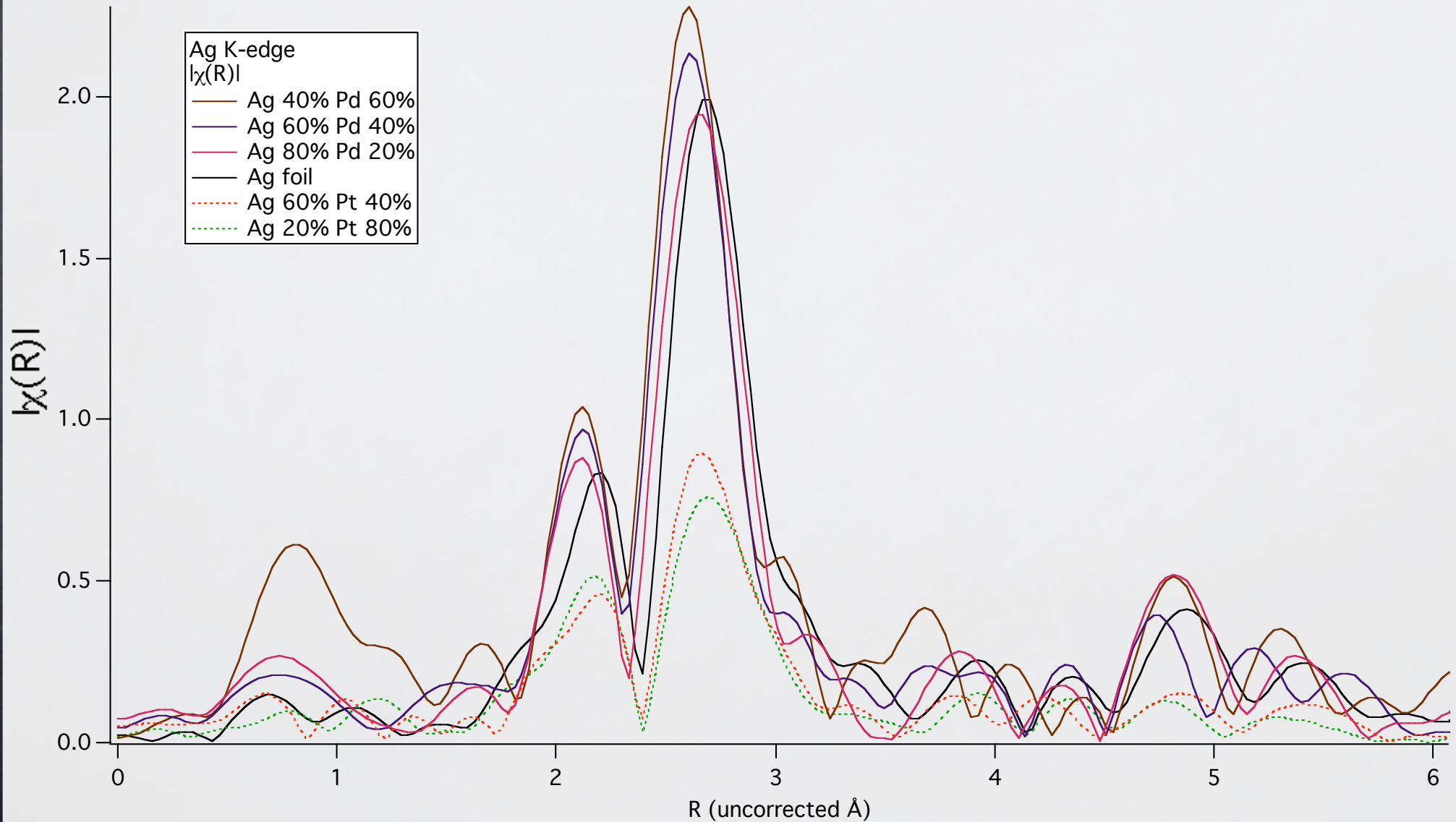
# Ag K-edge



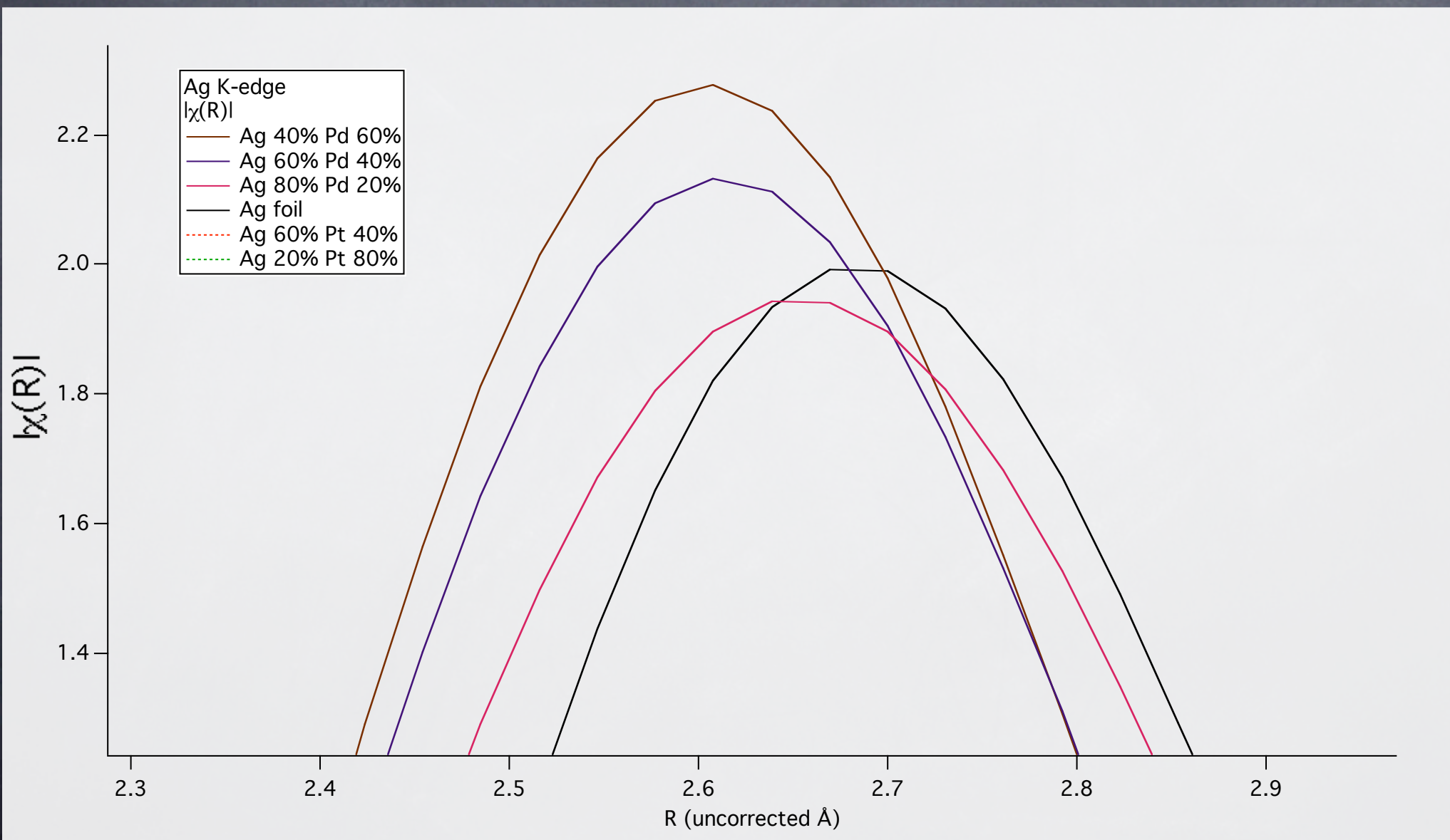
# Ag K-edge $\chi(k)$



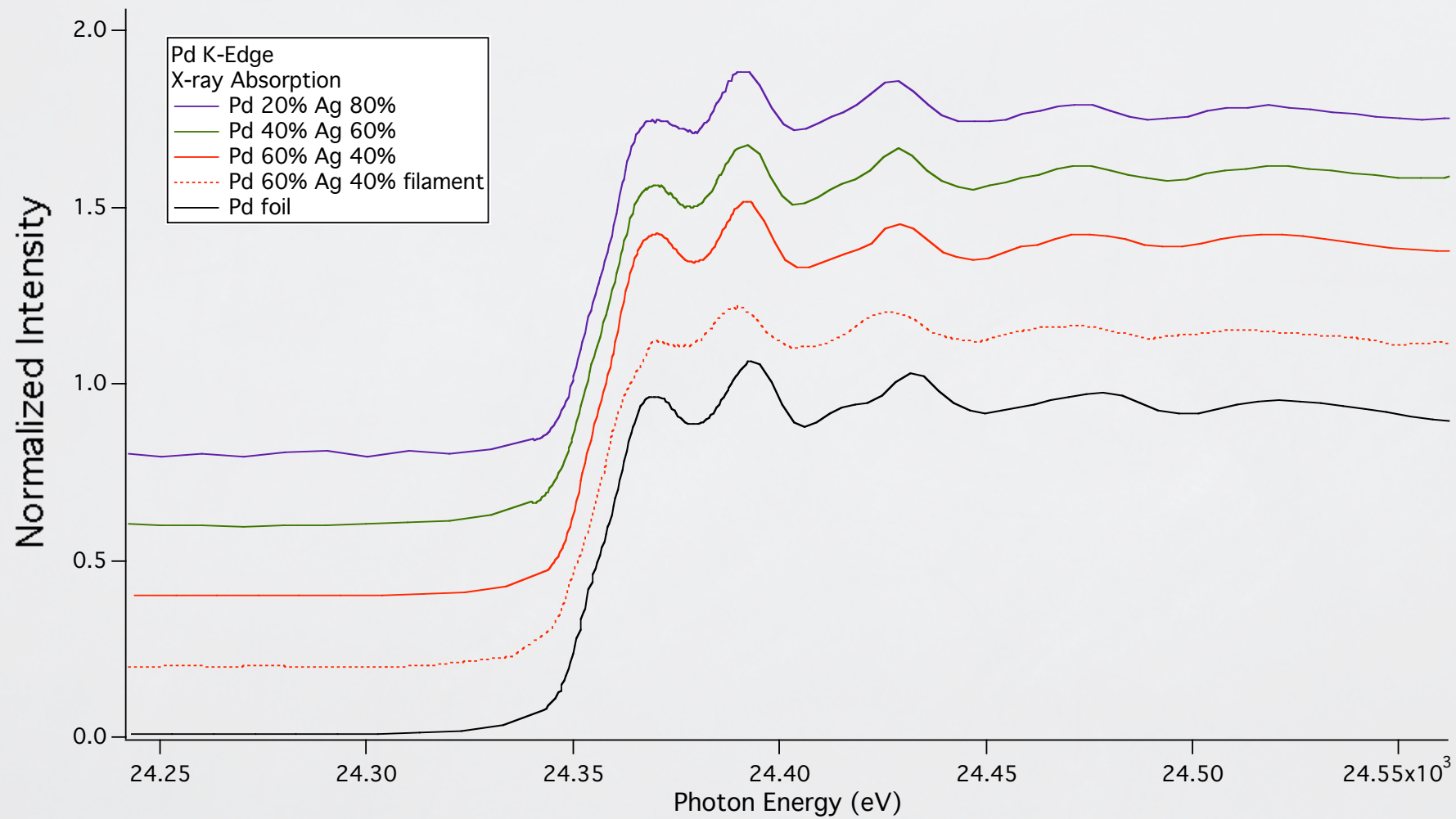
# Ag K-edge $\chi(r)$



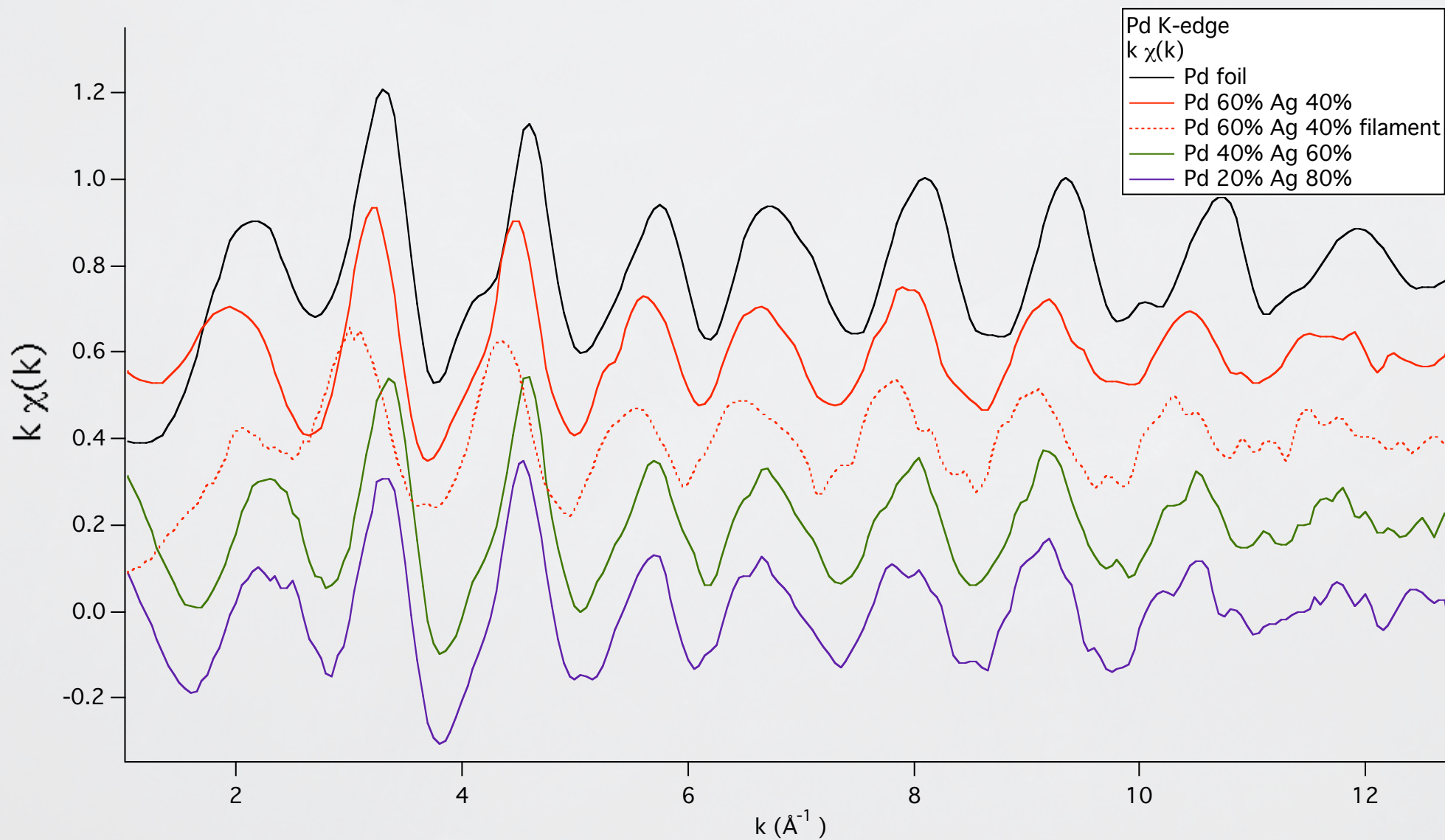
# Ag K-edge $\chi(r)$



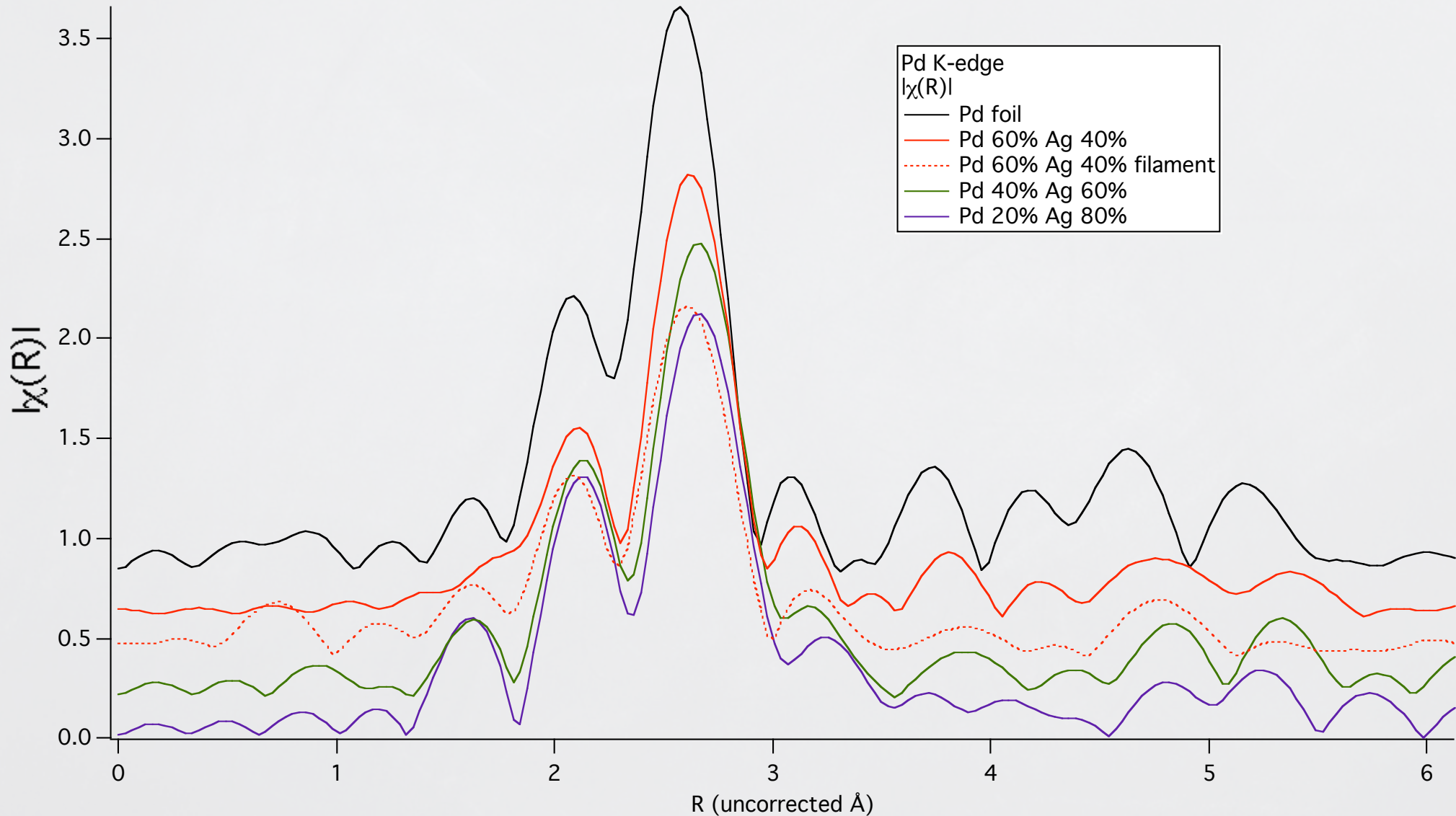
# Pd K-edge



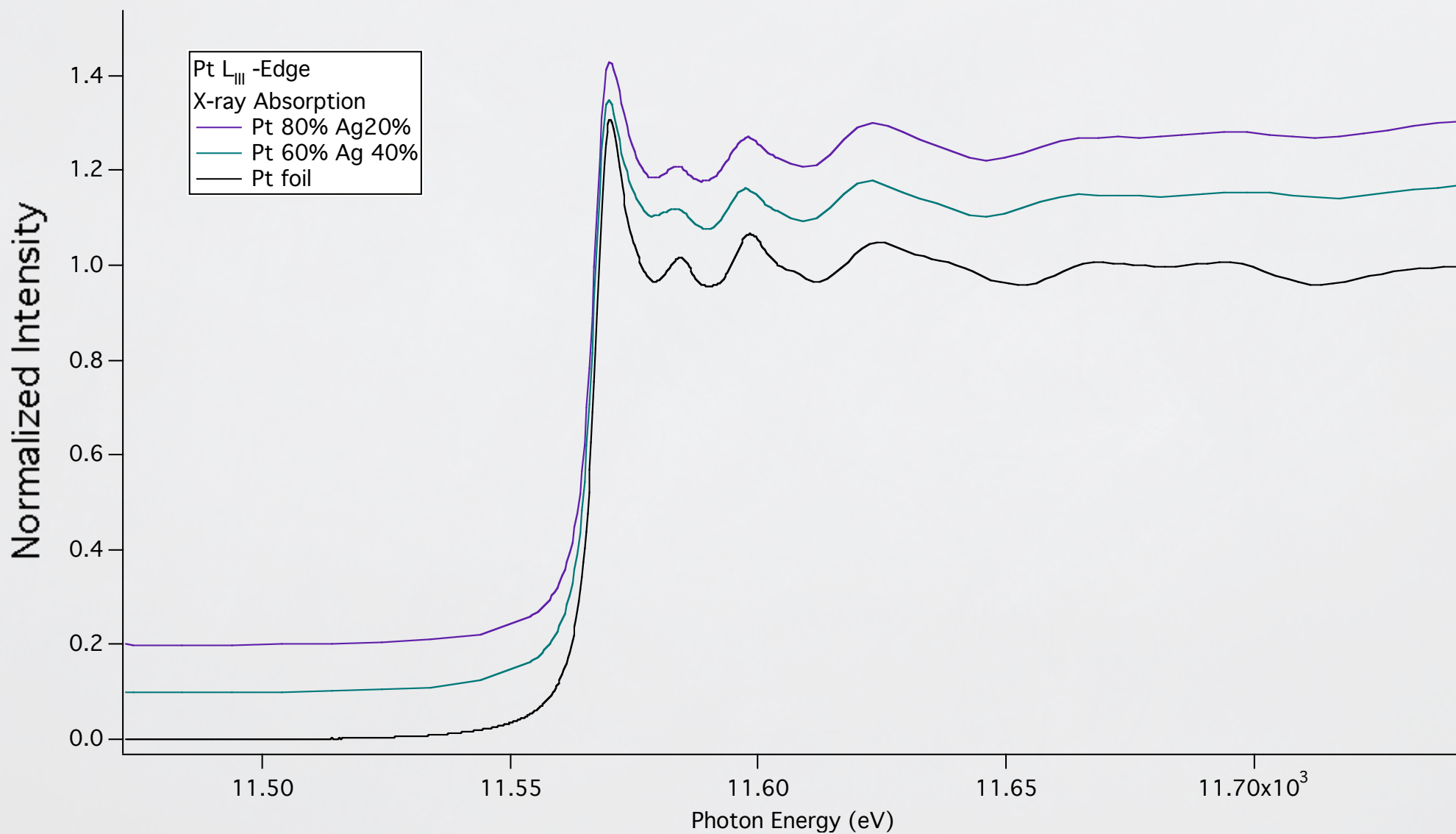
# Pd K-edge $\chi(k)$



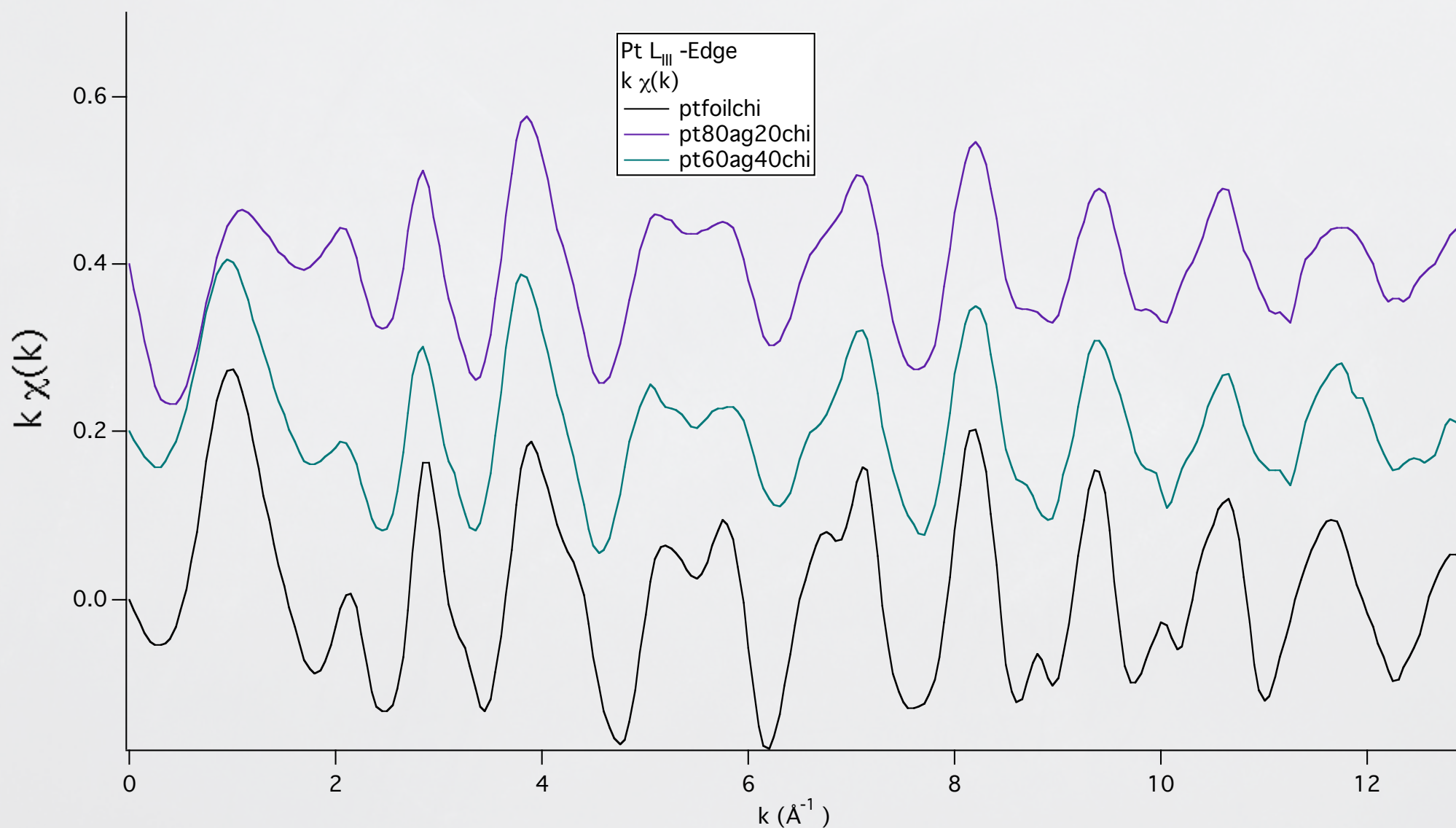
# Pd K-edge $\chi(R)$



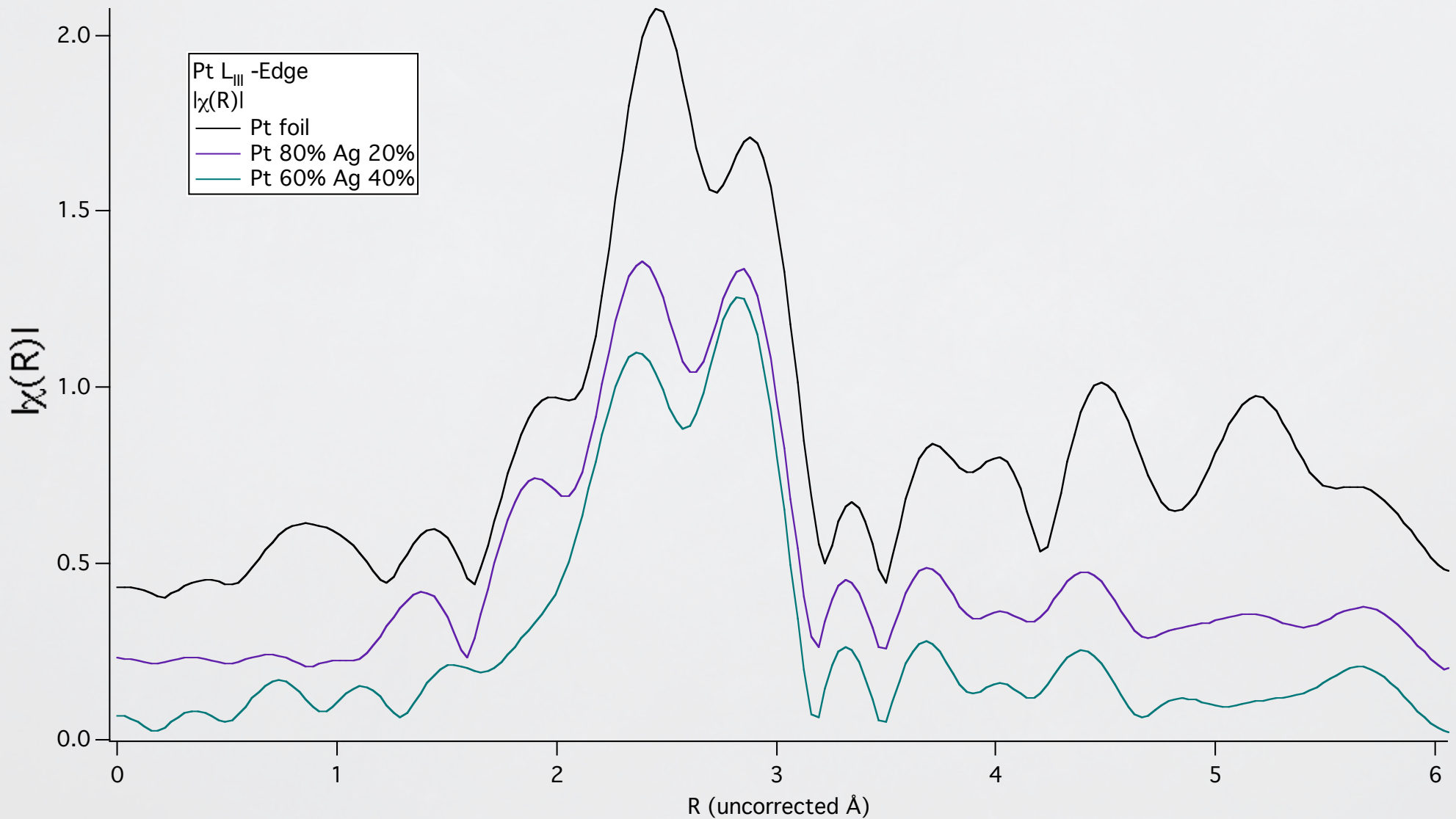
# Pt K-edge



# Pt K-edge $\chi(k)$



# Pd K-edge $\chi(R)$



# Qualitative Trends

- Ag Edge
  - AgPd Shorter Bond Length Trend
  - AgPt No Strong Trend
- Pd Edge
  - AgPd Longer Bond Length Trend
- Pt Edge
  - AgPt No Strong Trend

# Cluster Feff Calculations

- Feff 8.2 is a program designed to calculate the X-ray absorption spectrum of a system from 1st principles.
- It uses the Local Density Approximation method of Density Functional Theory to calculate self-consistent potentials that it uses to model electron scattering in a material.

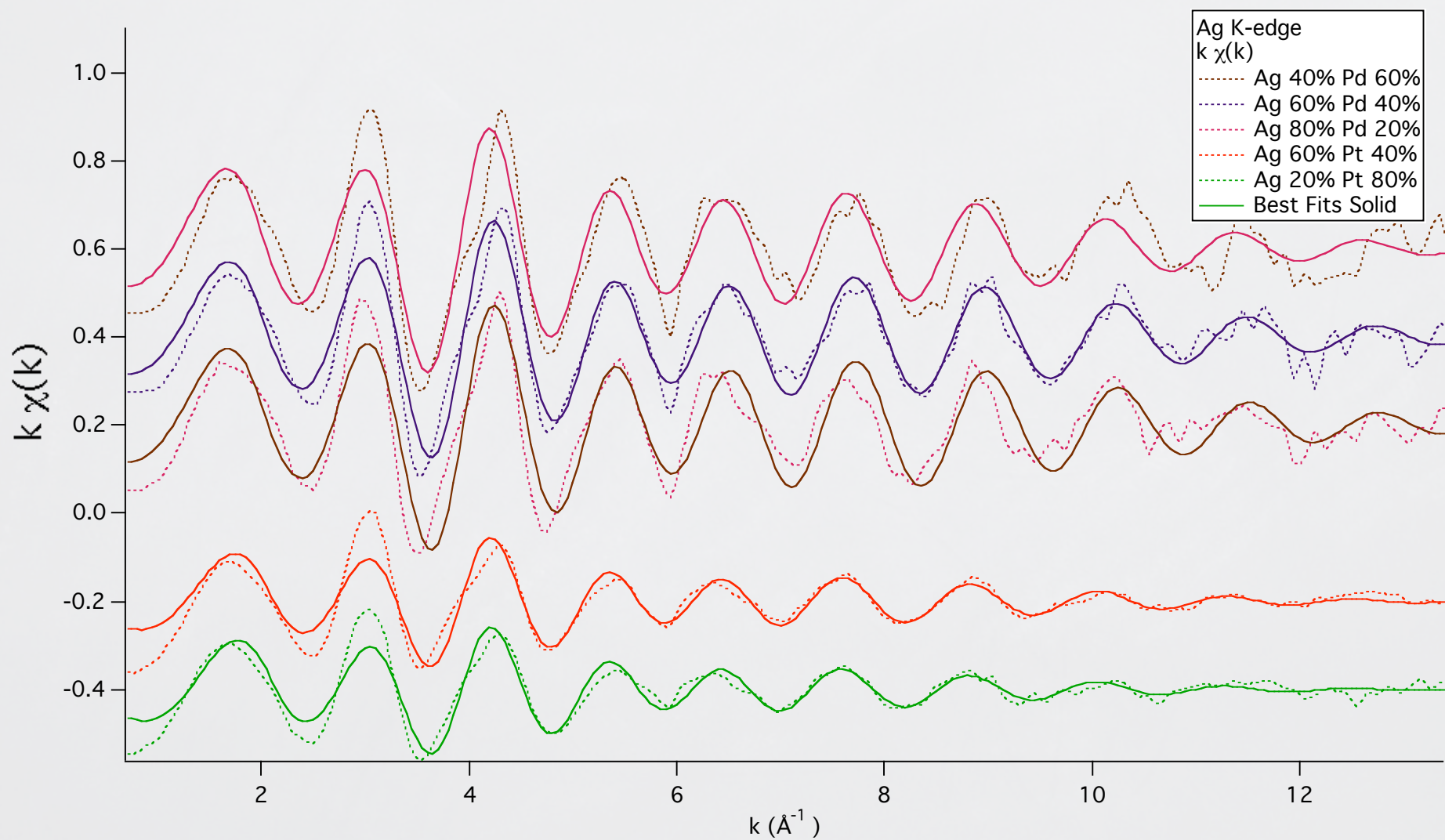
# Feff Calculations

- We must make assumptions about our system in order to model it with Feff.
- In the case of the AgX Clusters, we made the assumption that we could model the clusters by starting with Pd, Pt, and Ag crystals.
- We substituted the proposed alloy material into a perfect crystal and calculated the expected scattering paths.

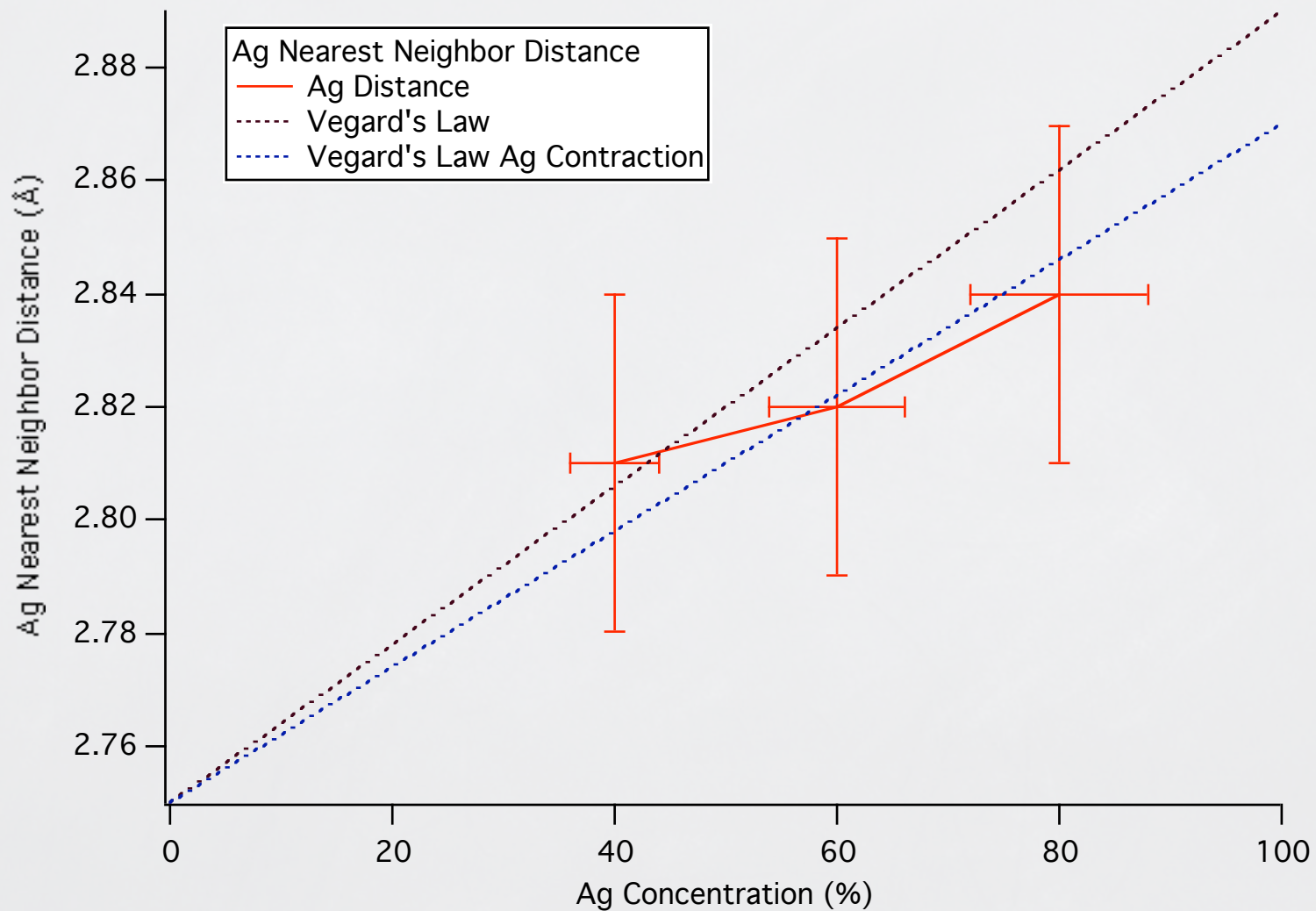
# Feff Fitting of Expt DATA

- We fit the experimental data to determine bond lengths from both directions to determine and approximate error in our measurements.
- Typically, the error that this directional fitting introduced was  $0.03\text{\AA}$ .

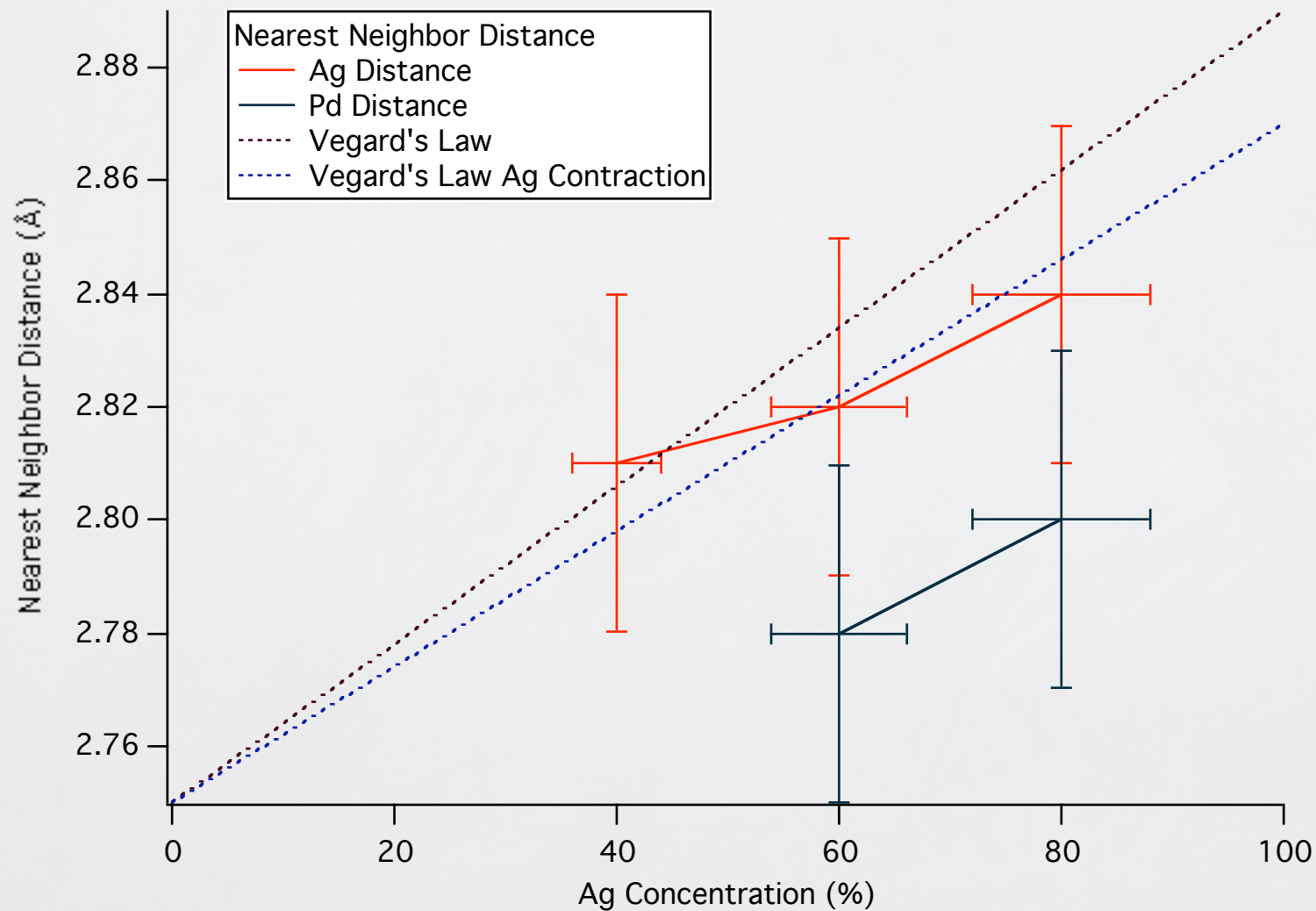
# Fitting Ag



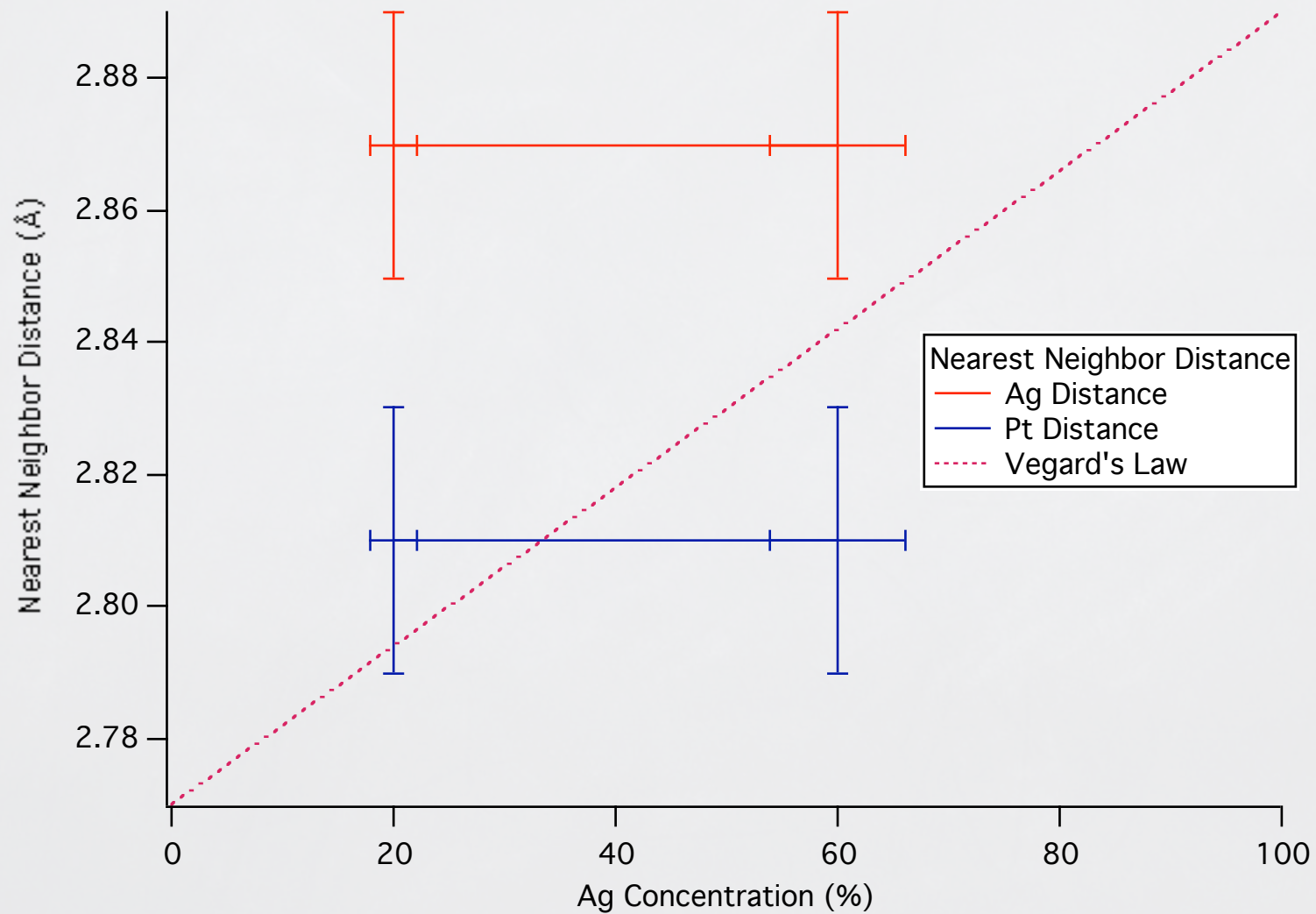
# AgPd Fit Results



# PdAg Fit Results



# AgPt



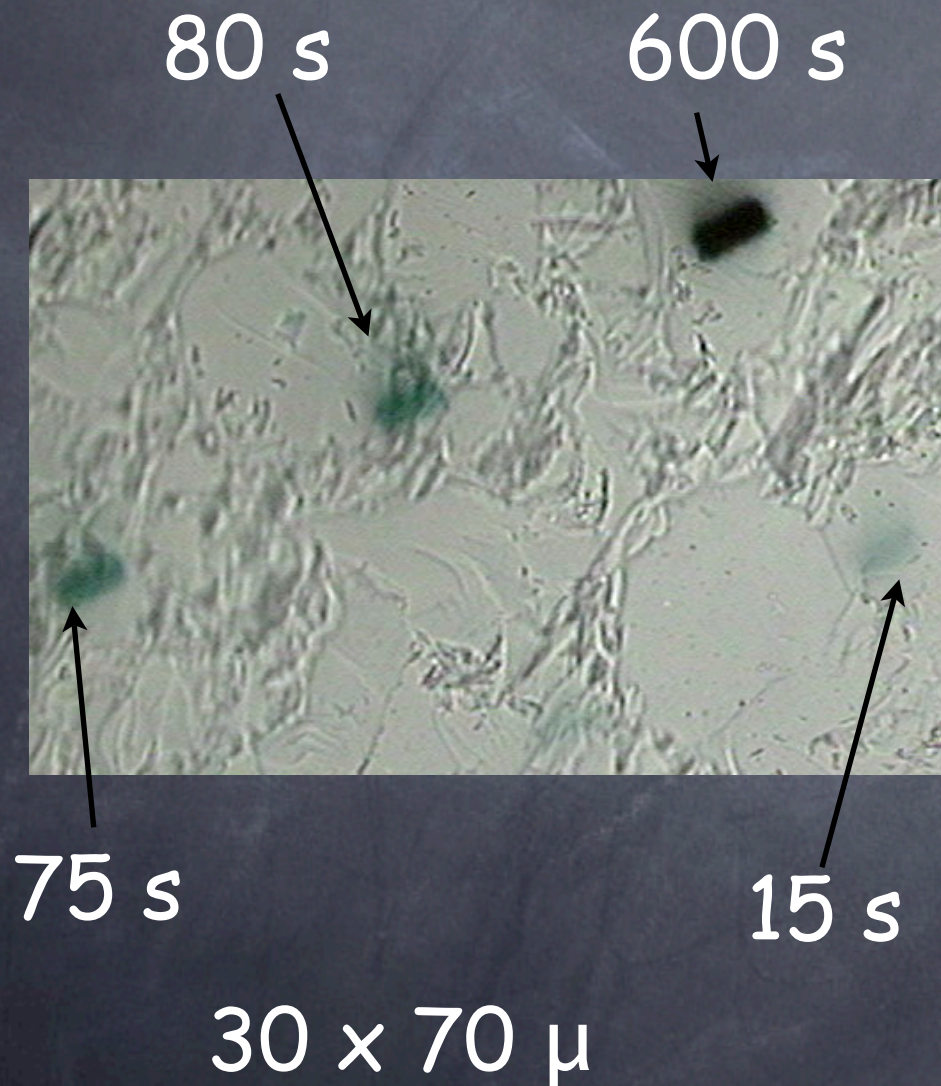
# Dielectric Devices

- Create nanowires in aerogels.
- Aerogels are non-conductive.
- Aerogels are great thermal insulators.
- Aerogels mainly  $\text{SiO}_2$ .

# Tailor Properties

- Soak aerogel with  $\text{AgNO}_3$  in 2-propanol.
- Irradiate with highly-collimated X-ray beam.
- Irradiations as low as 30 s cause the formation of conductive arrays of Ag nanoclusters.

# Example

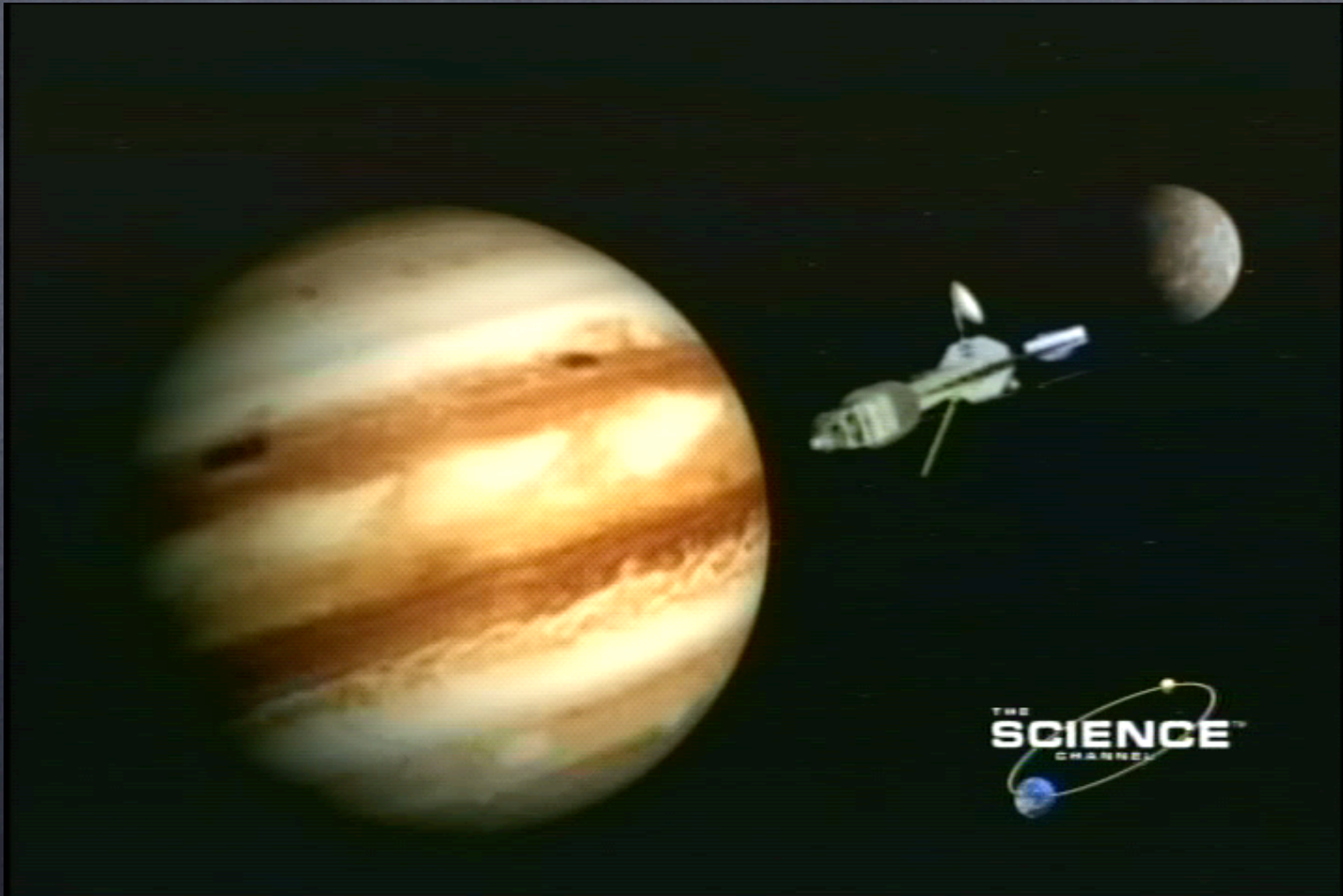


# Conclusions

- Rule out alloying in AgPt system.
- Very Confident of alloying in AgPd system.
- Possible local segregation of Pd in AgPd system reducing average near-neighbor length.
- Create wires of nanoparticles in dielectric materials to tailor properties.

# Radiation Damage

- Many reasons to be interested in radiation damage. One of the most important to me is:



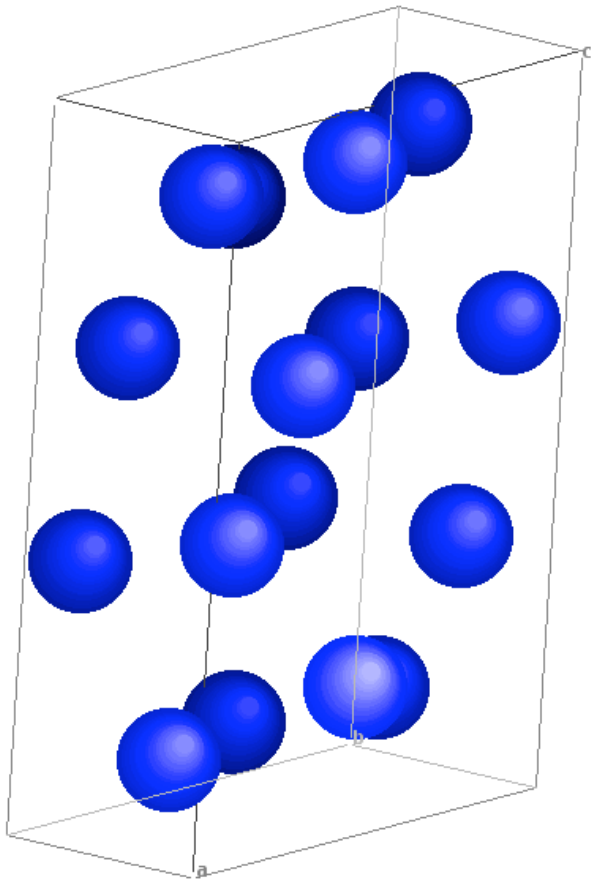
# Radiation Damage

- Many reasons to be interested in radiation damage. One of the most important to me is:
  - Space Travel
- I will illustrate how the synchrotron techniques can be used to study radiation damage with Pu alloys and Spinel

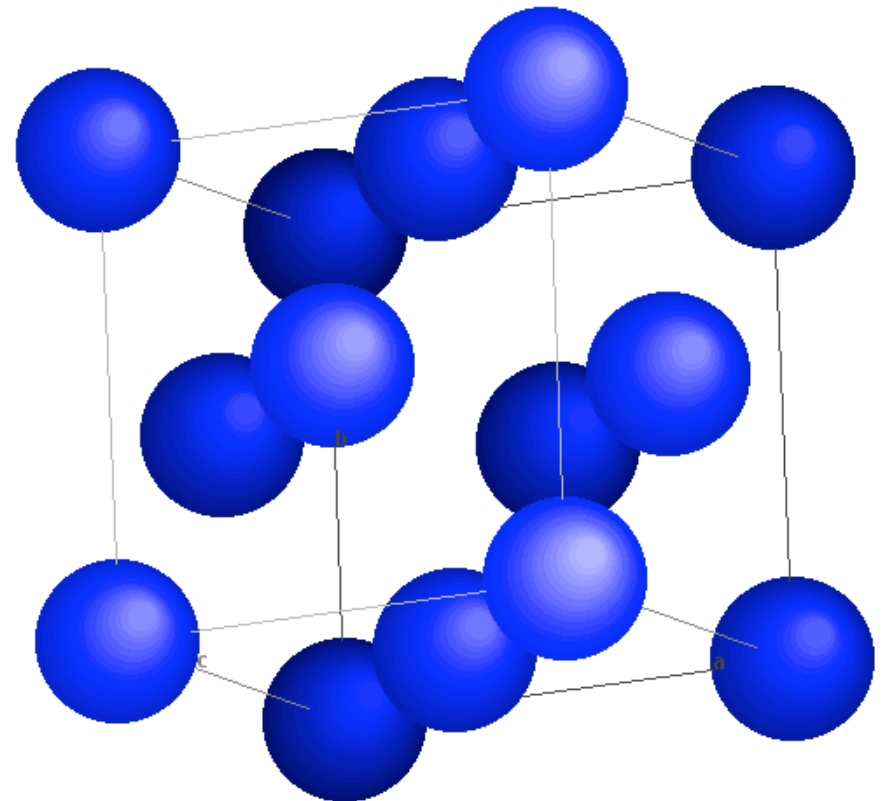
# Pu CRYSTAL STRUCTURES

- The Plutonium phase diagram is complex between 25 C and 600 C plutonium undergoes 5 phase transitions.

Alpha (monoclinic)



Delta (face-centered cubic)



# SAMPLE PREPARATION

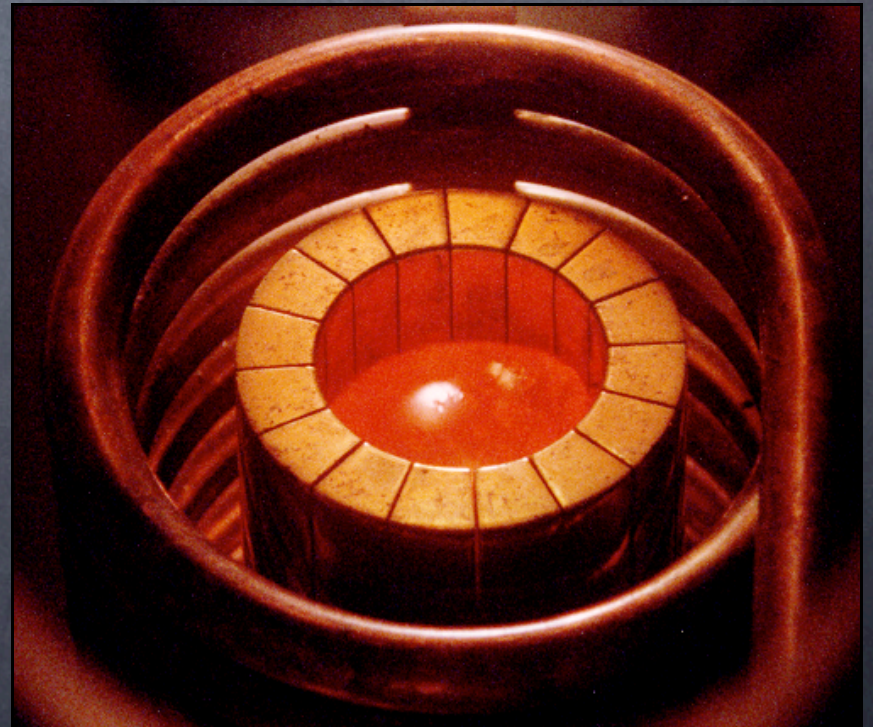
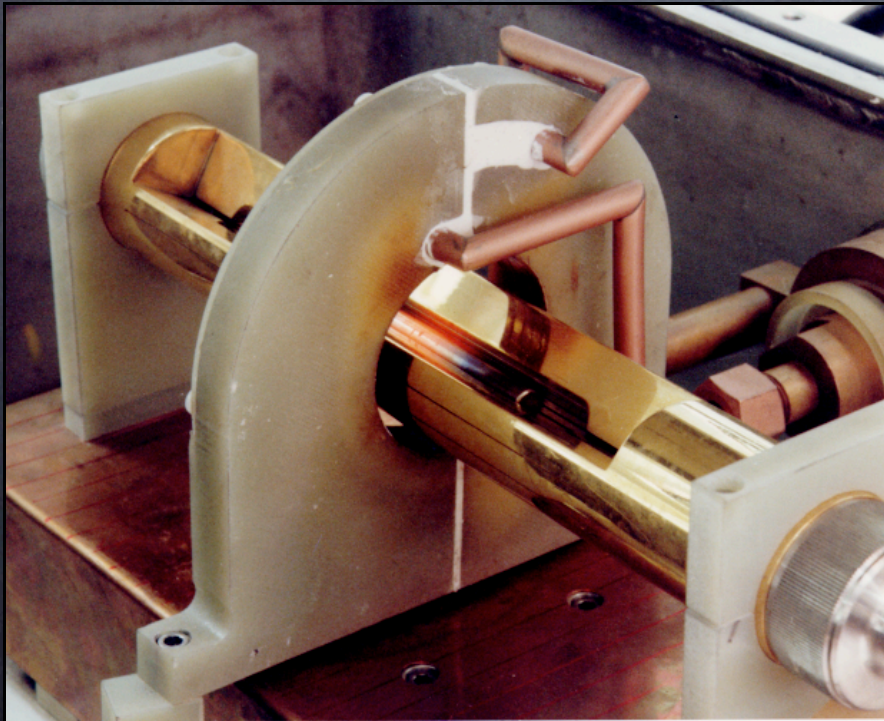
- Levitation Zone Refinement

- 1.5 cm/min Zone Travel Rate

- 800 °C Molten Zone (red glow)

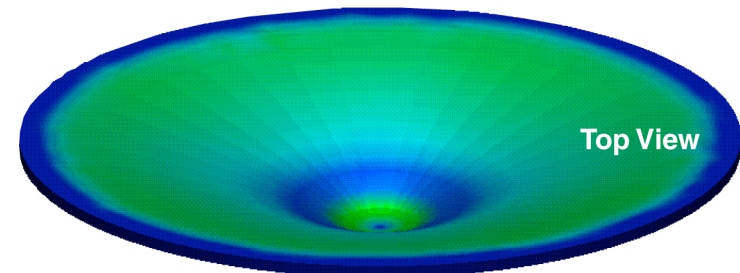
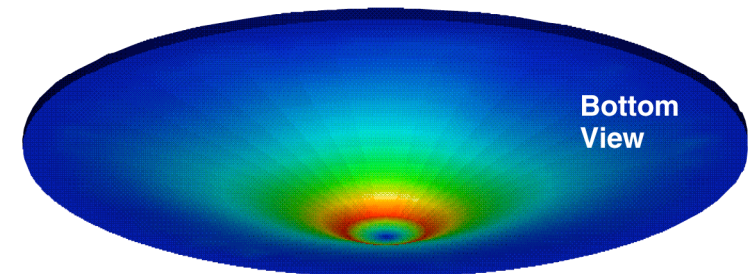
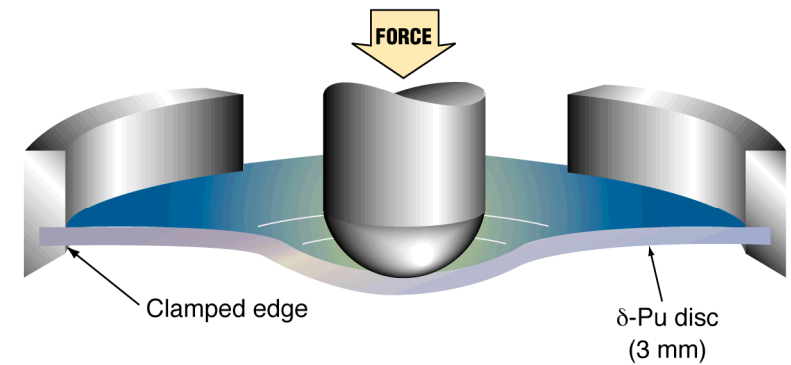
- Levitation Distillation

- 180 ppm Impurities



# STRAIN ANNEALING

- Solid State Crystal Growth
  - Deform Metal (Strain)
  - Heat (Anneal)
- Grain Growth Predominates
  - Net Increase of Grain Size



## LANL

- Repeated Sputter-Anneal Cycles to Remove Dissolved  $O_2$
- Samples Transferred to Vacuum Transfer Vessel

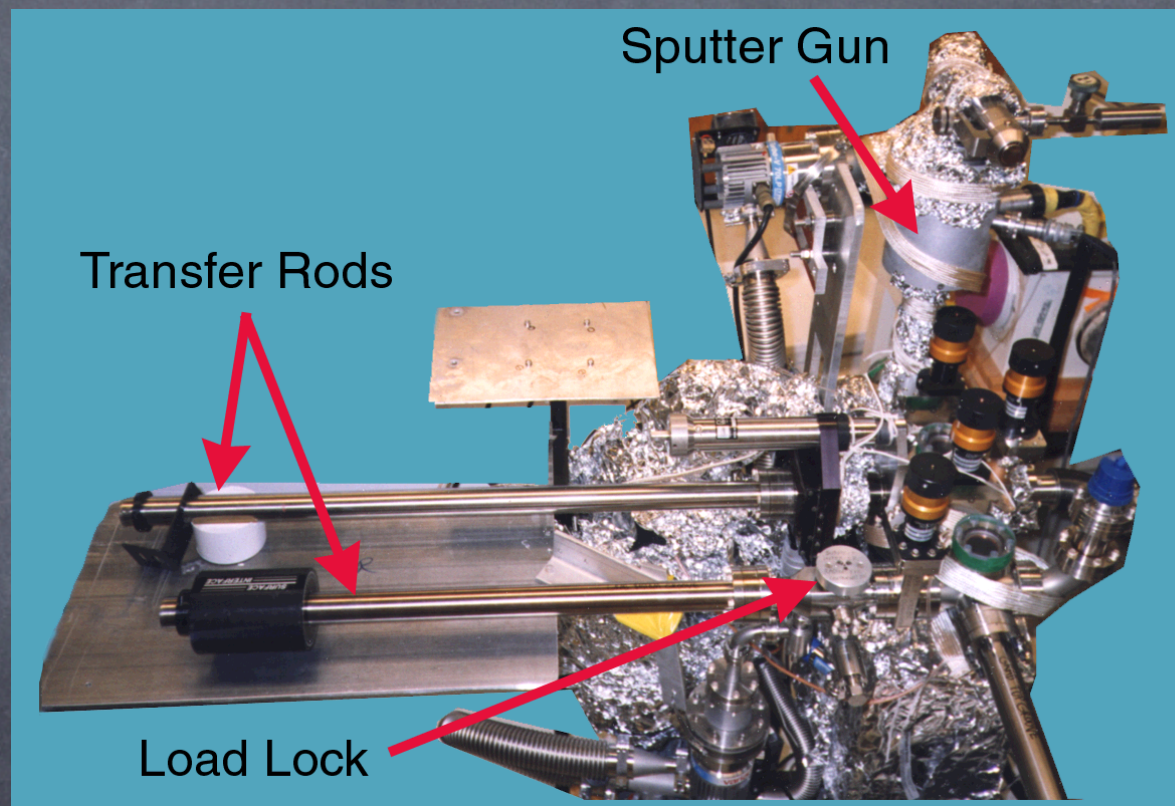
## Shipping

- Samples Shipped in Vacuum Transfer Vessel at  $10^{-8}$  Torr

## ALS

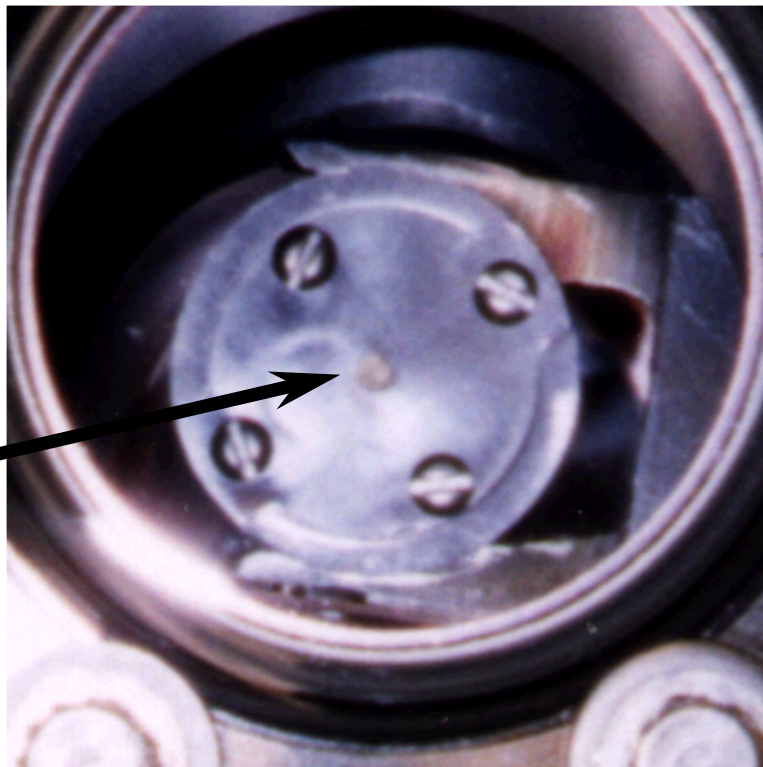
- Final Cleaning Done in Sample Handling and Integrated Transfer System for Pu Intense Light Experiments
  - Sputter 5 kV Ar ions
  - Anneal 75 °C

# SURFACE PREPARATION



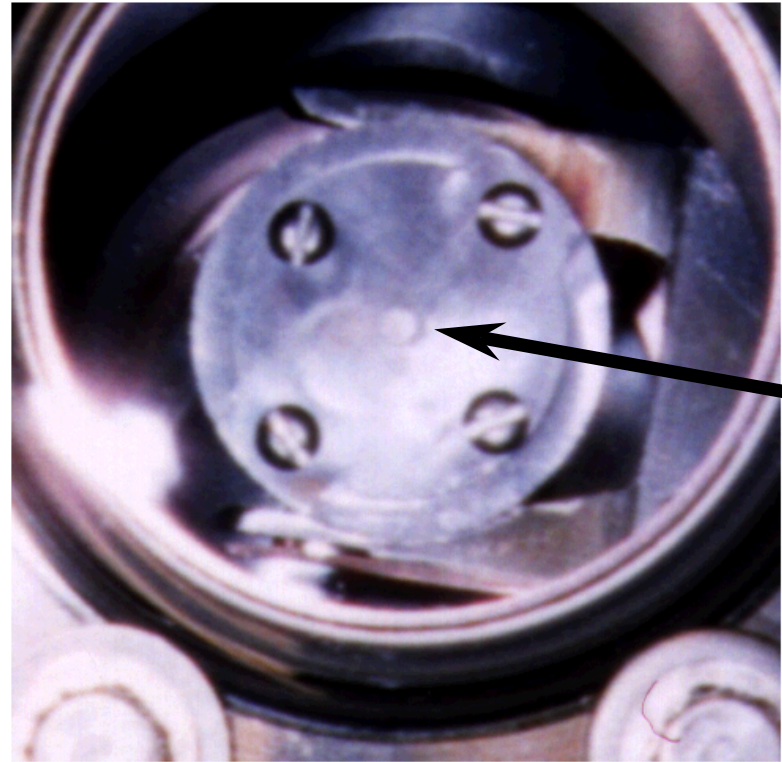
# SPUTTER CLEANING

- Sputtering Removes Surface Contamination
- Annealing Removes Sputter Induced Defects



Plutonium  
Disk

**Before Sputter**

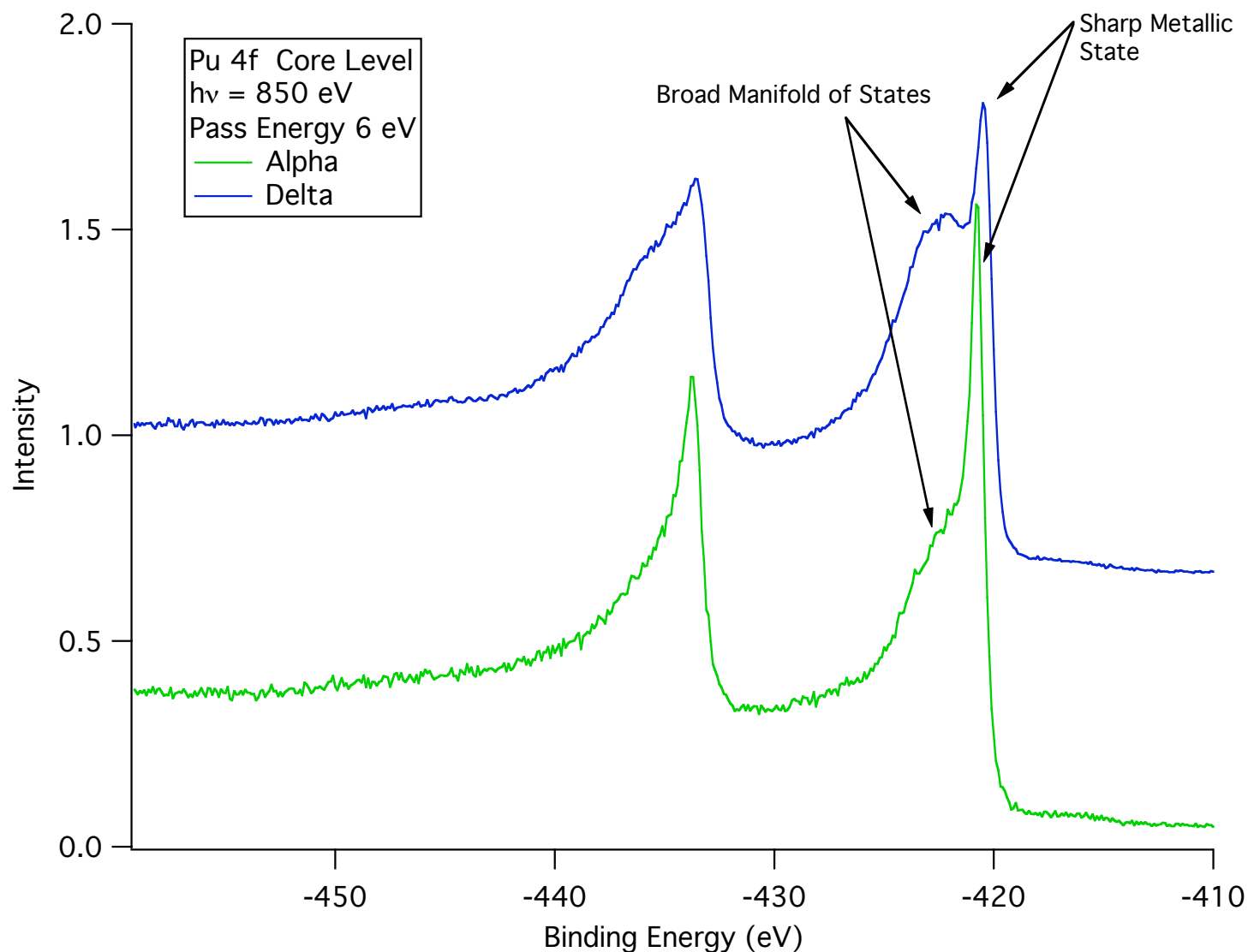


Plutonium  
Disk

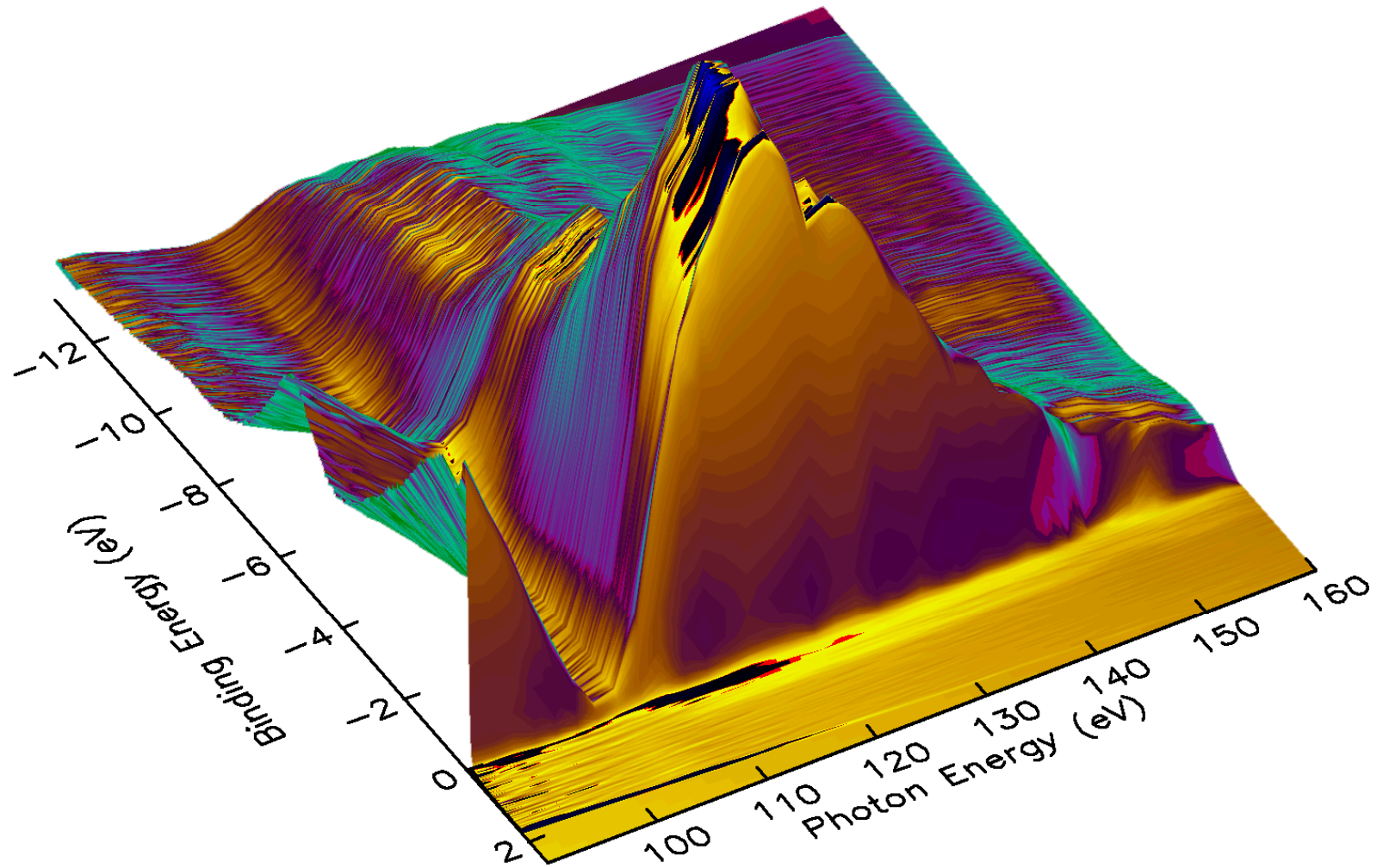
**After Sputter**

# Pu CORE LEVEL PES

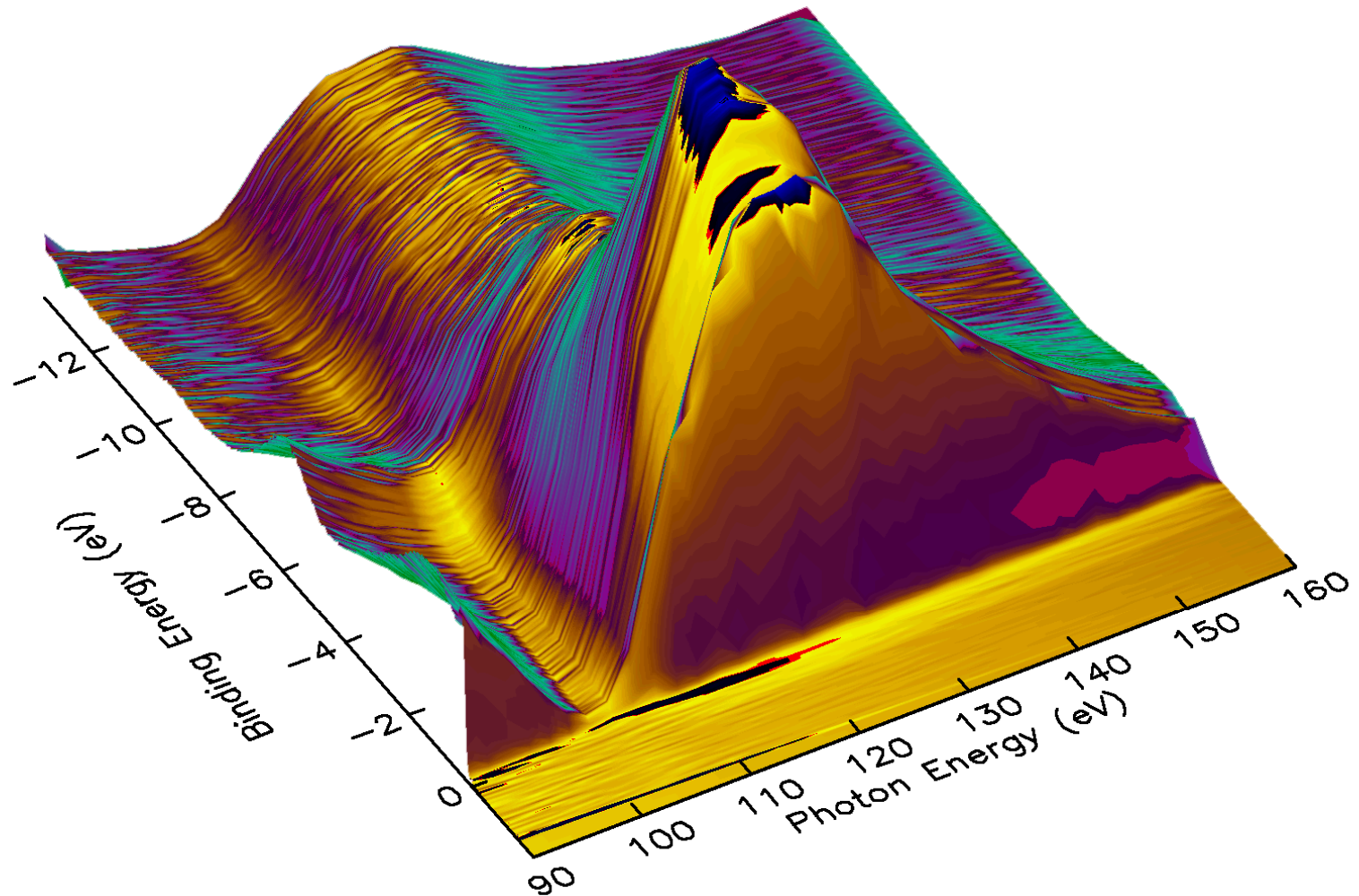
## 4f Core Level Photoemission



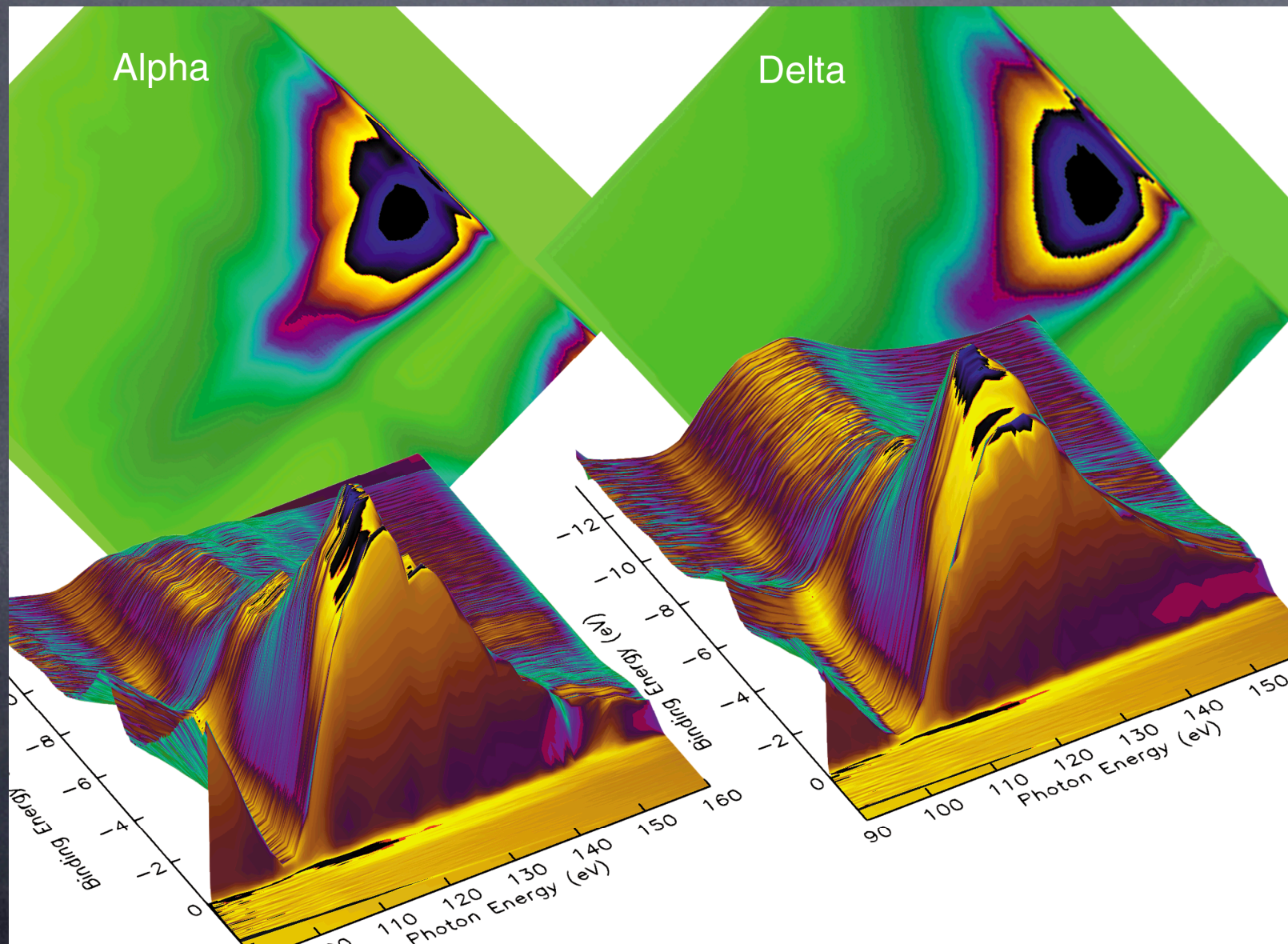
# ALPHA RESPES



# DELTA RESPES



# RESPES



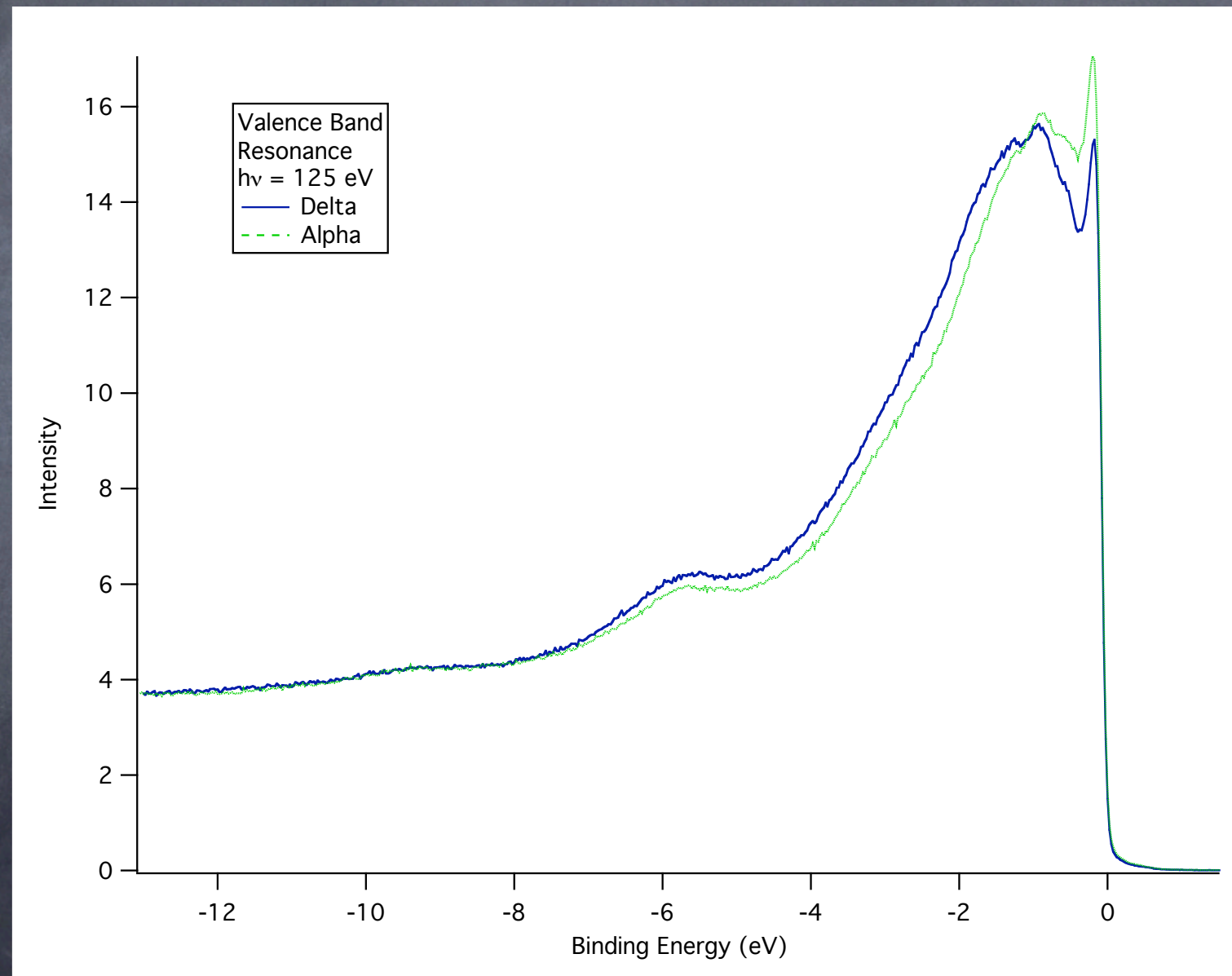
# VALENCE BAND

- Density of States

- Alpha more density near  $E_f$

- Delta more density at higher binding energy away from  $E_f$

- Consistent with localization of f-electrons in Delta



# Band Theory

- Band Structure

- Density Functional Theory

- $n(r) = |\Psi(R)|^2$

- Assume  $n(r) = \sum |\psi(r)|^2$

- LDA assume slowly varying  $n(r)$

- Correlated Electron Effects

- $E_{\text{tot}} = E_{\text{LDA}} [n_{\text{itin}} + n_{\text{loc}}] + \Delta E_{\text{corr}} [n_{\text{loc}}]$

- $n_{\text{loc}} = 4$

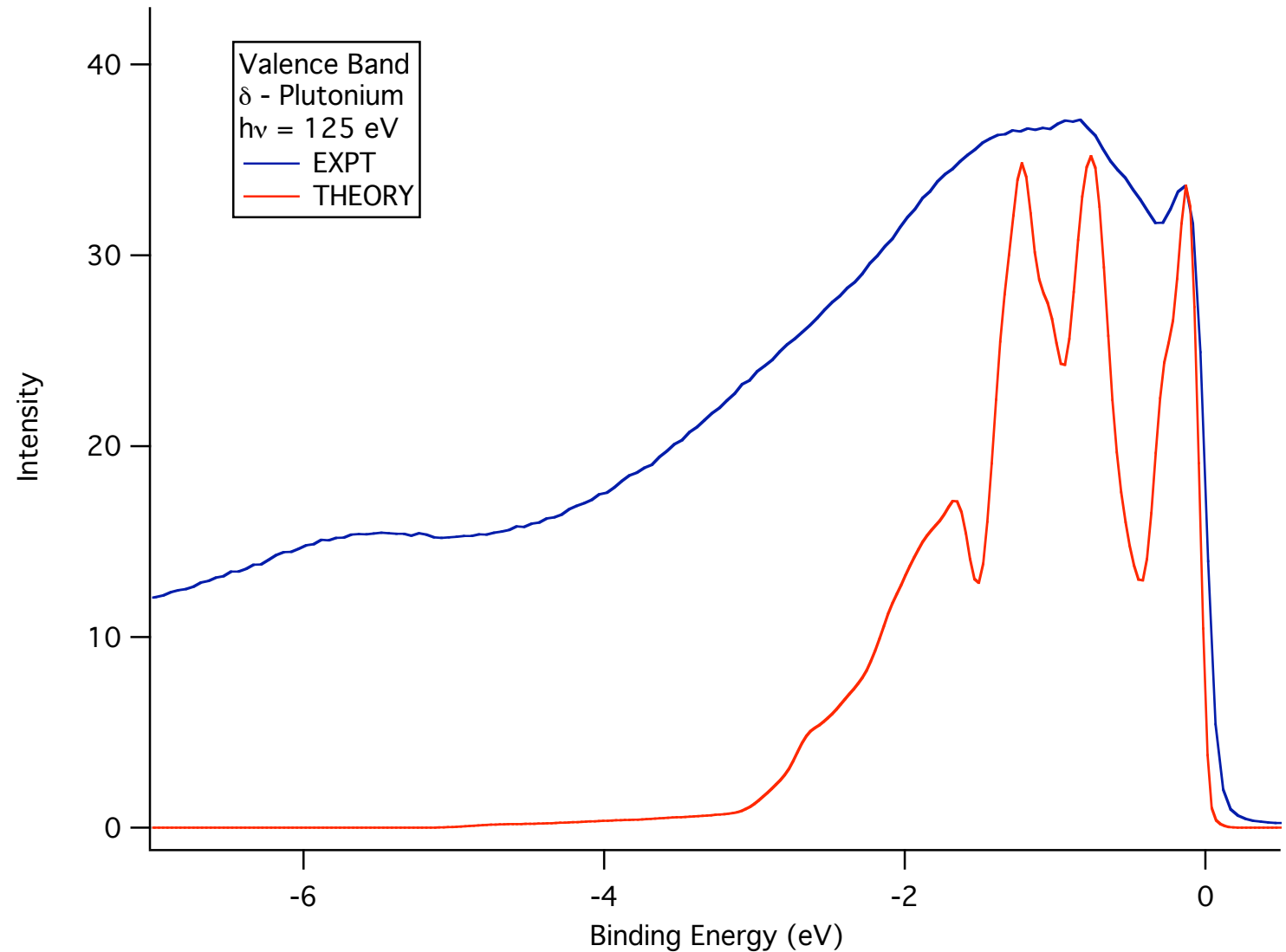
# DELTA THEORY

- Density of States

- 4 localized 5f electrons

- Good Agreement

- Theory Missing One Peak at ~0.5 eV
  - Photoemission Matrix Elements NOT Accounted for in Calculation



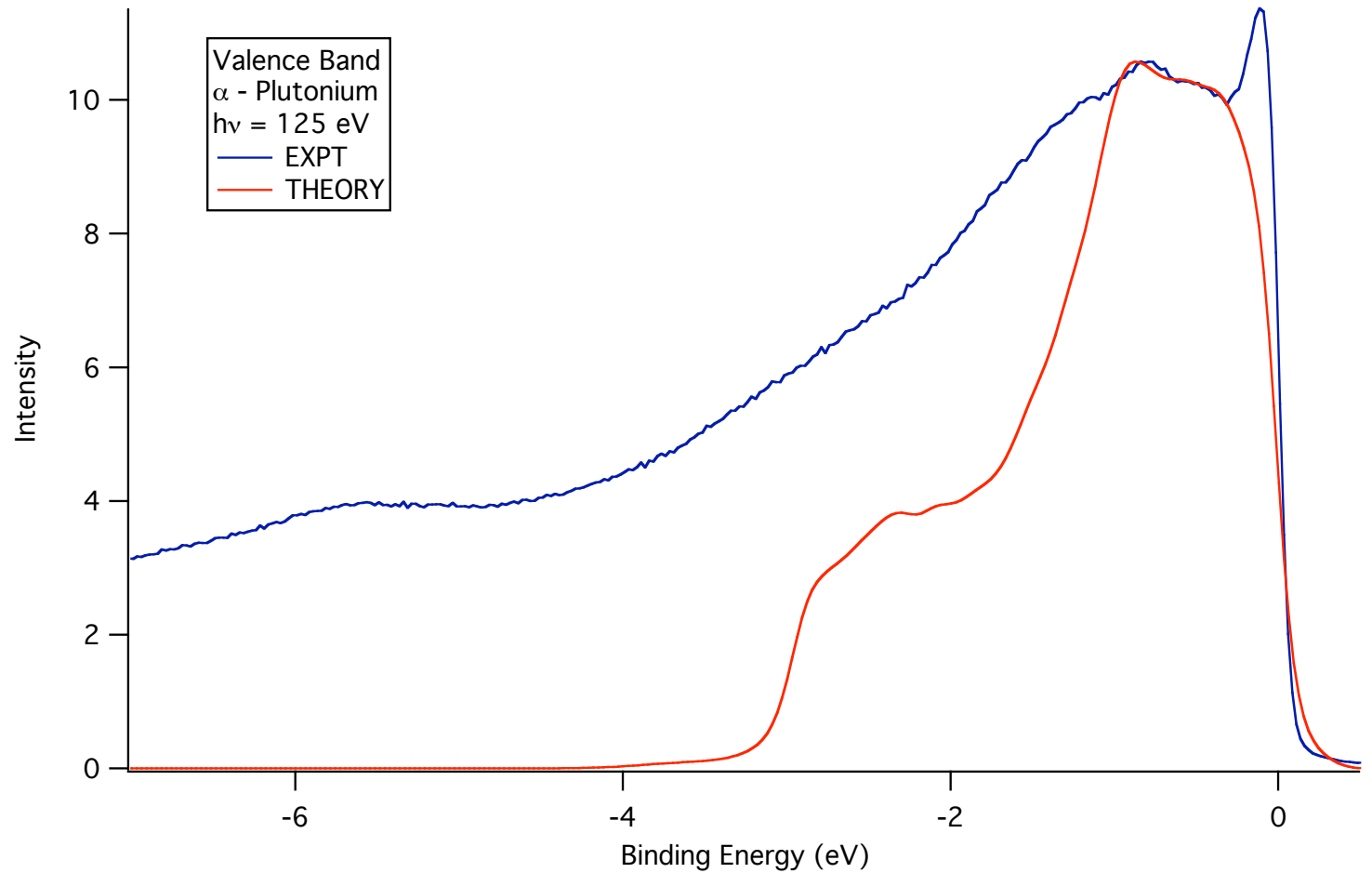
# ALPHA THEORY

- Density of States

- All 5f electrons itinerant

- Good Agreement

- Theory Missing One Peak at  $E_f$
  - Photoemission Matrix Elements NOT Accounted for in Calculation



# ResPes Theory

- Resonant Photoemission

- Atomic Calculation

- Resonant Channel

$$\langle 5d^{10}5f^5 | r | 5d^9 5f^6 \rangle \rightarrow \langle 5d^9 5f^6 | e^2 / r | 5d^{10} 5f^4 + e^- \rangle$$

- Direct Channel

$$\langle 5d^{10} 5f^5 | r | 5d^{10} 5f^4 + e^- \rangle$$

- Interference  
between the two  
channels gives rise  
to resonant  
photoemission

- Fano Parameter (q)

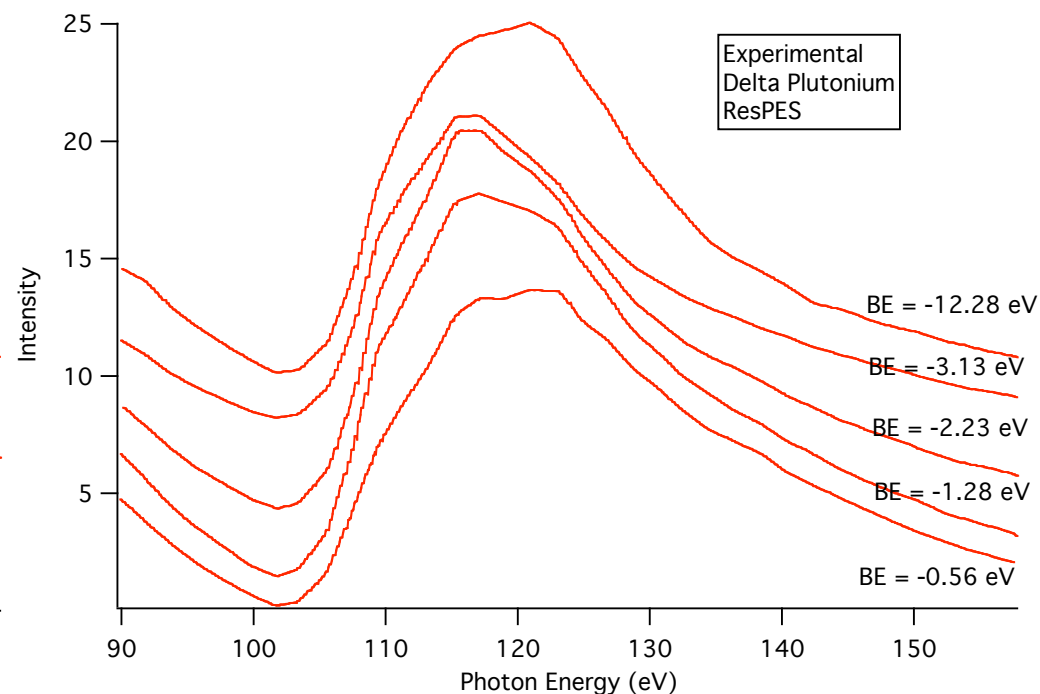
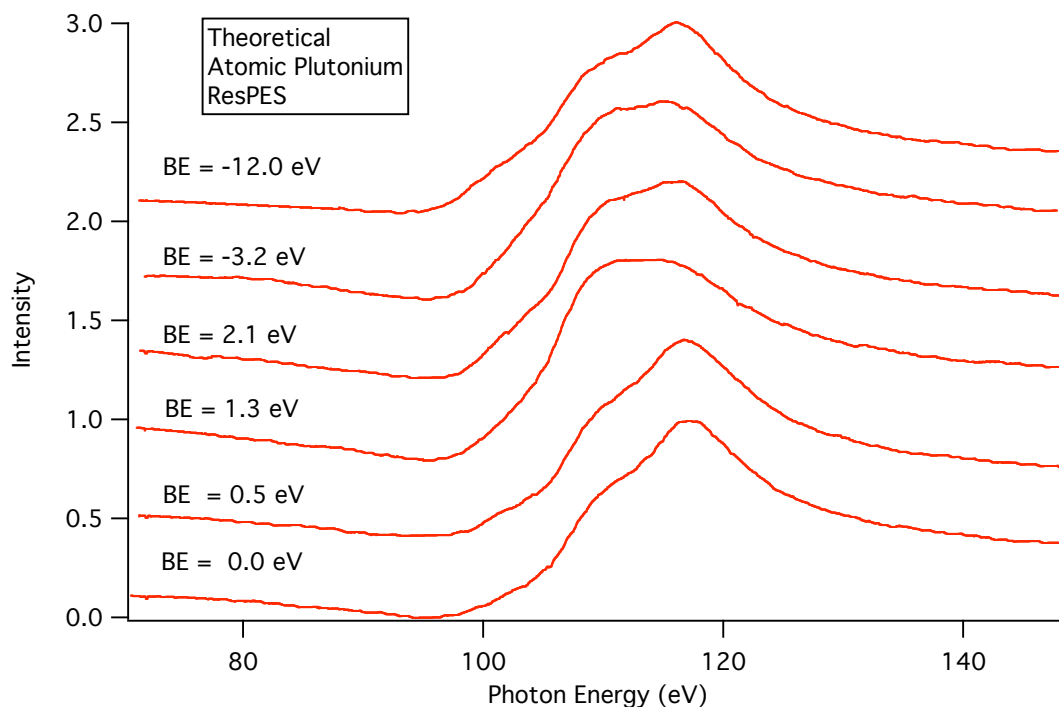
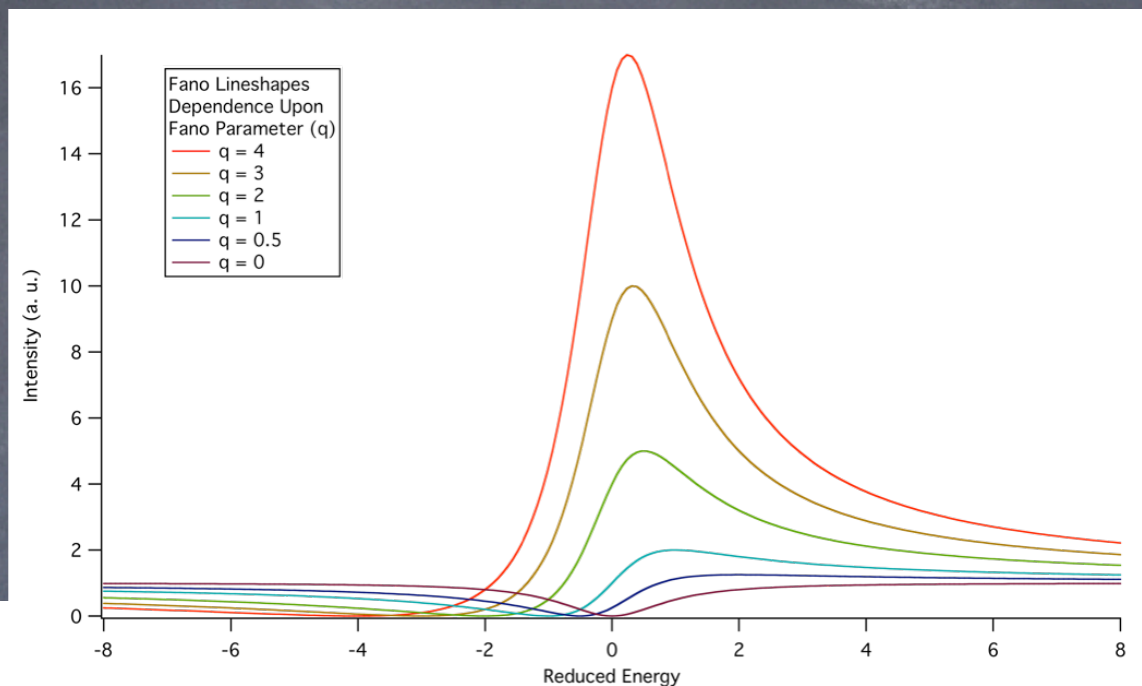
$$q \sim \langle 5d^{10} 5f^5 | r | 5d^9 5f^6 \rangle / \langle 5d^{10} 5f^5 | r | 5d^{10} 5f^4 + e^- \rangle$$

# Pu RESPES

● Resonant  
Photoemission

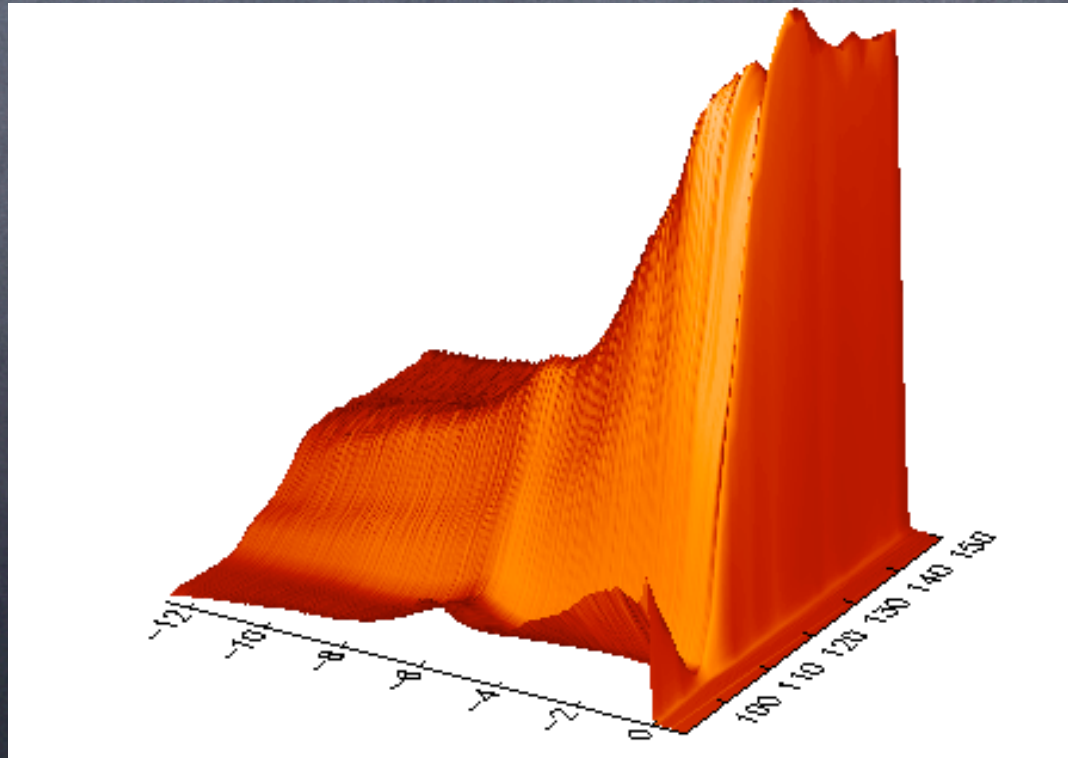
● Atomic Calculation

● 5d 5f 5f



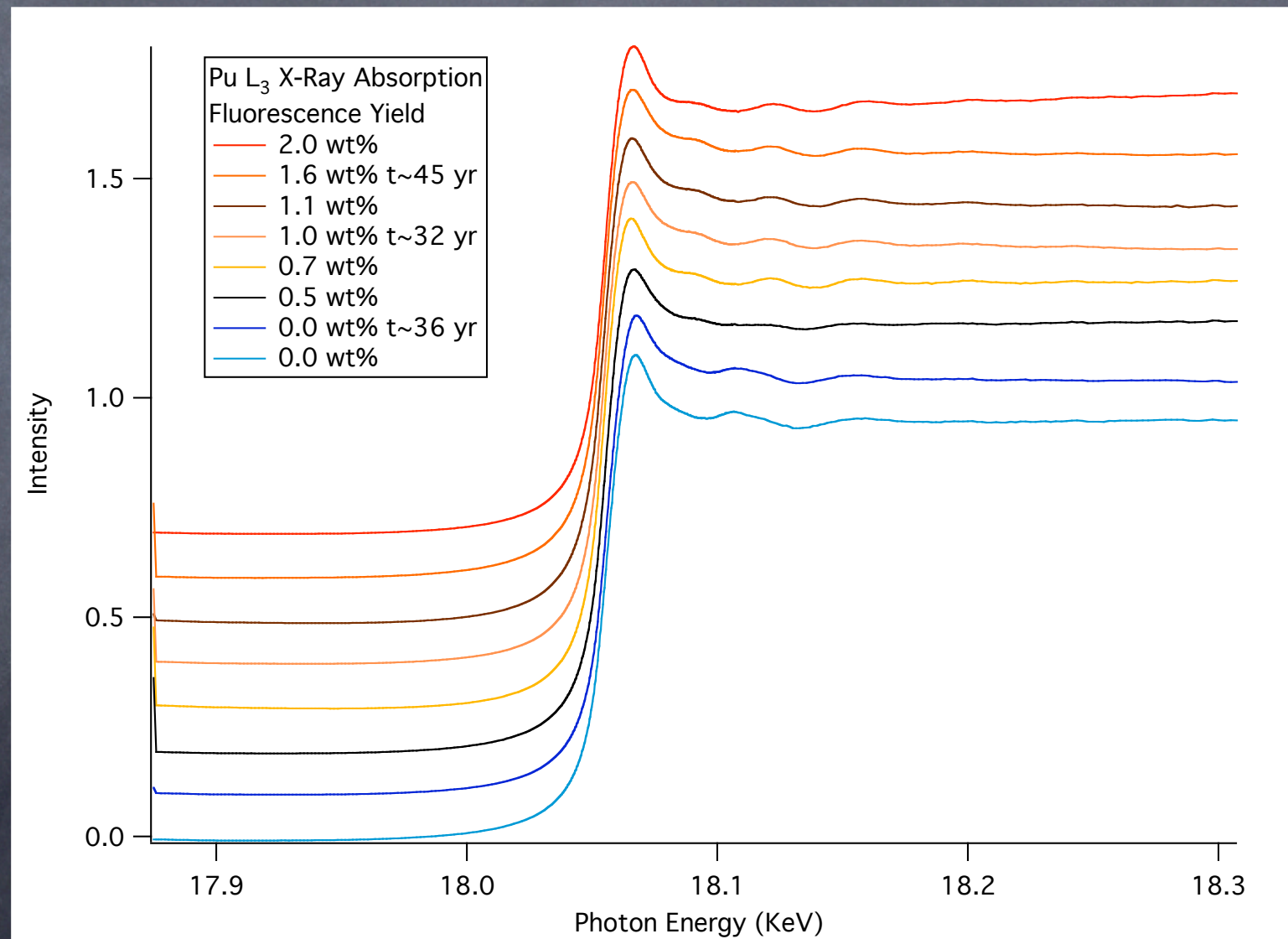
# Radiation Damage???

- Science Based Stockpile Stewardship
  - 38 year-old Plutonium
  - Lineshape similar to  $\delta$ -Pu
  - High Energy Oscillatory Structure similar to  $\alpha$ -Pu

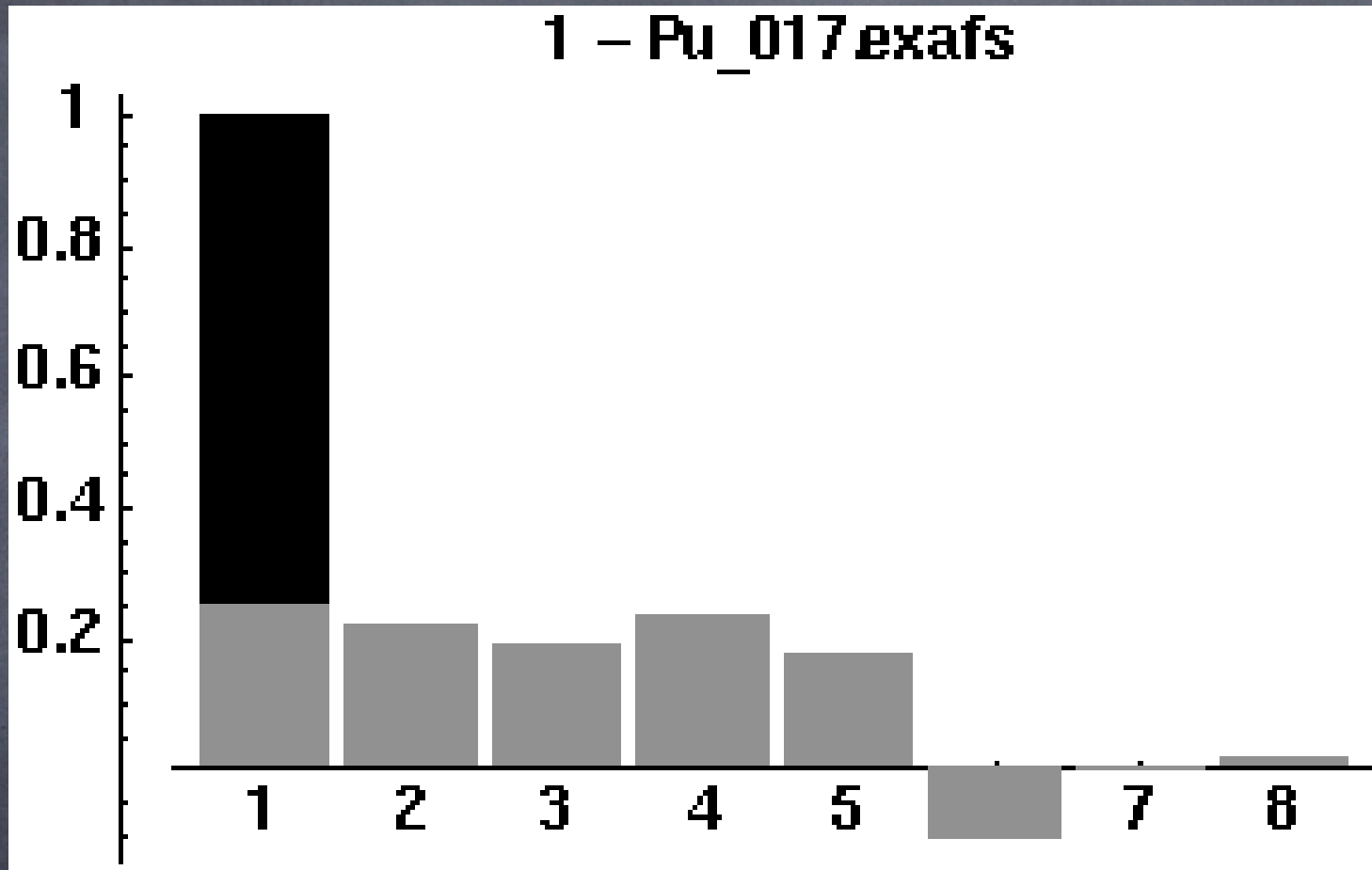


# Pu L<sub>3</sub> Absorption Edge

- F-Yield
- Bulk Measurement
- Self-Absorption
- Gallium Concentration
- Sample Age



# UNIQUENESS TESTING



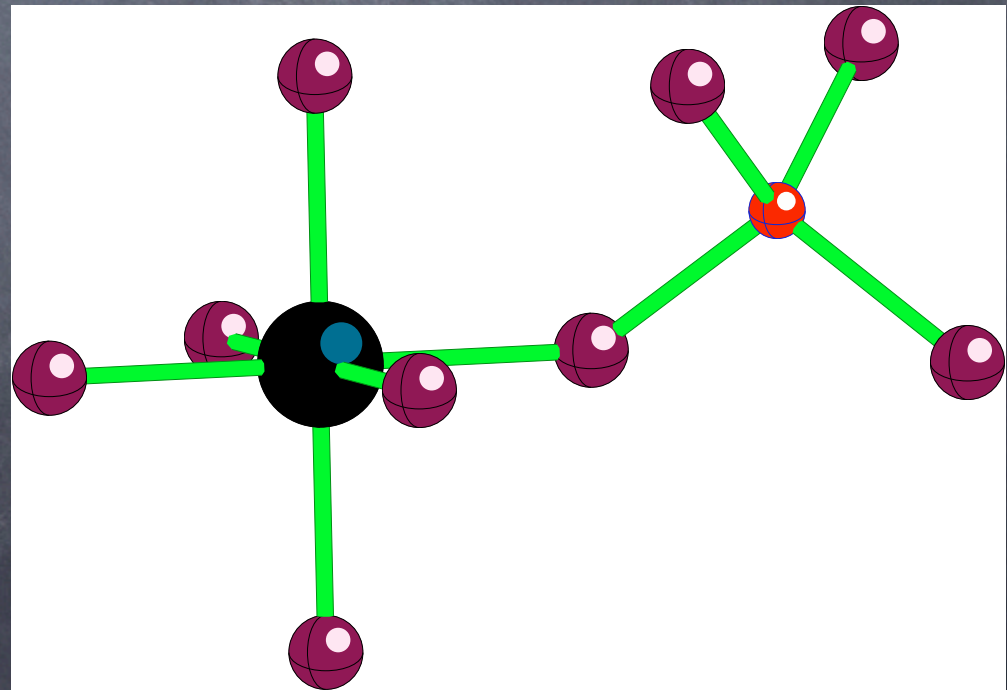
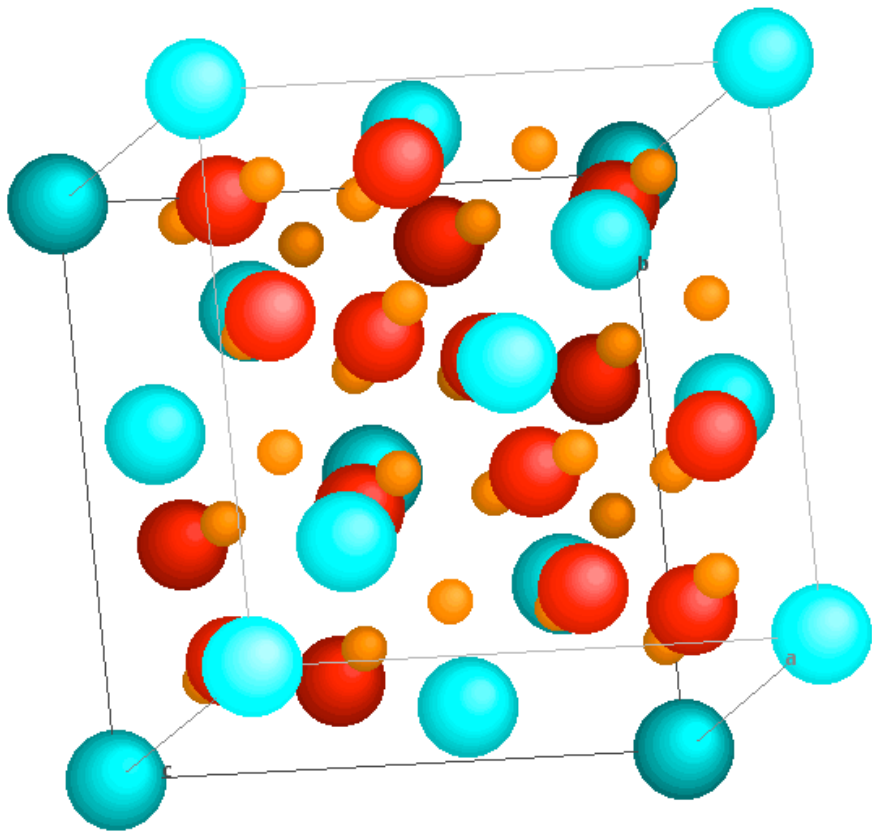
● 0.5 wt% Ga unusual

# RADIATION DAMAGE



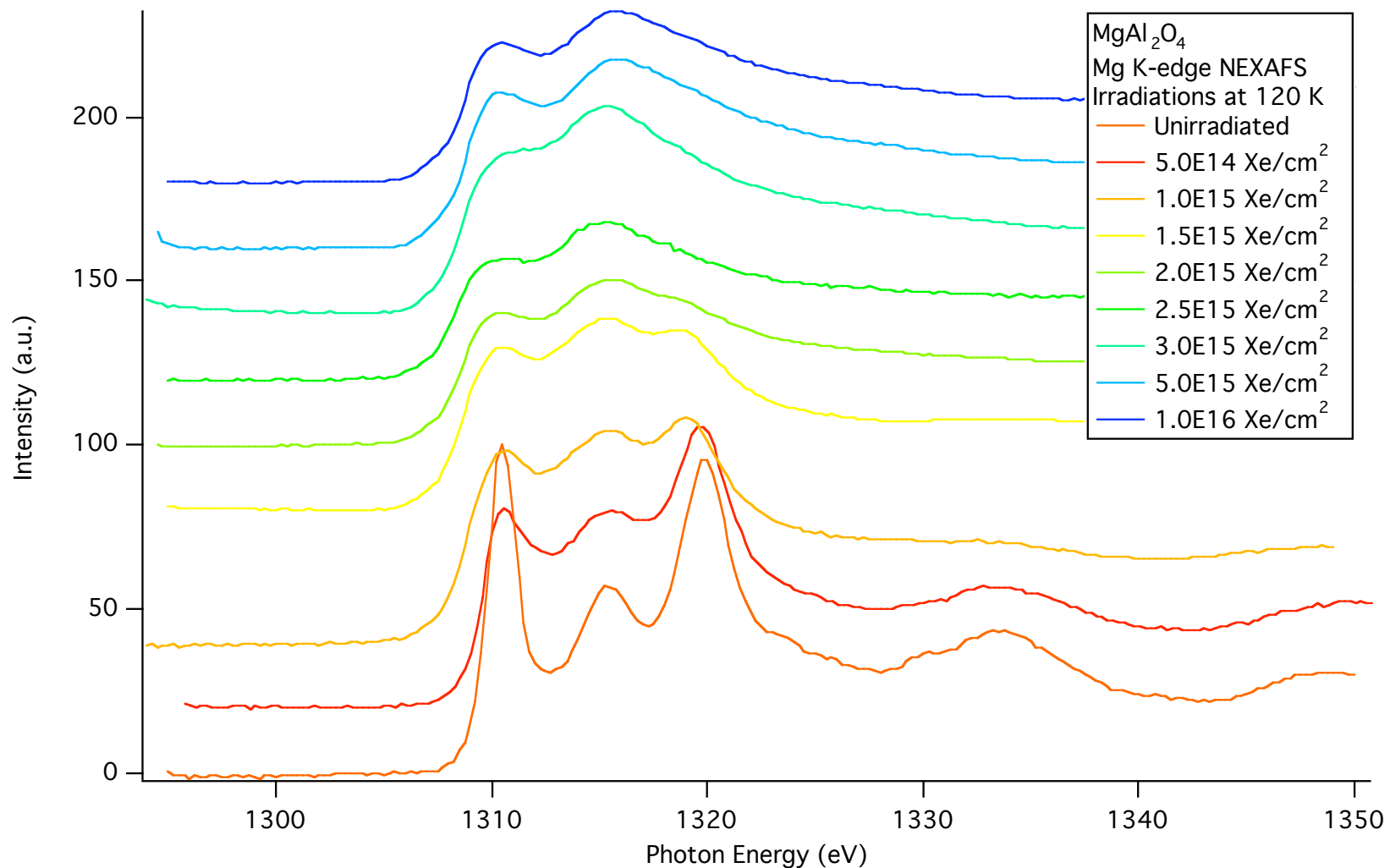
- Al octahedral

- Mg tetrahedral

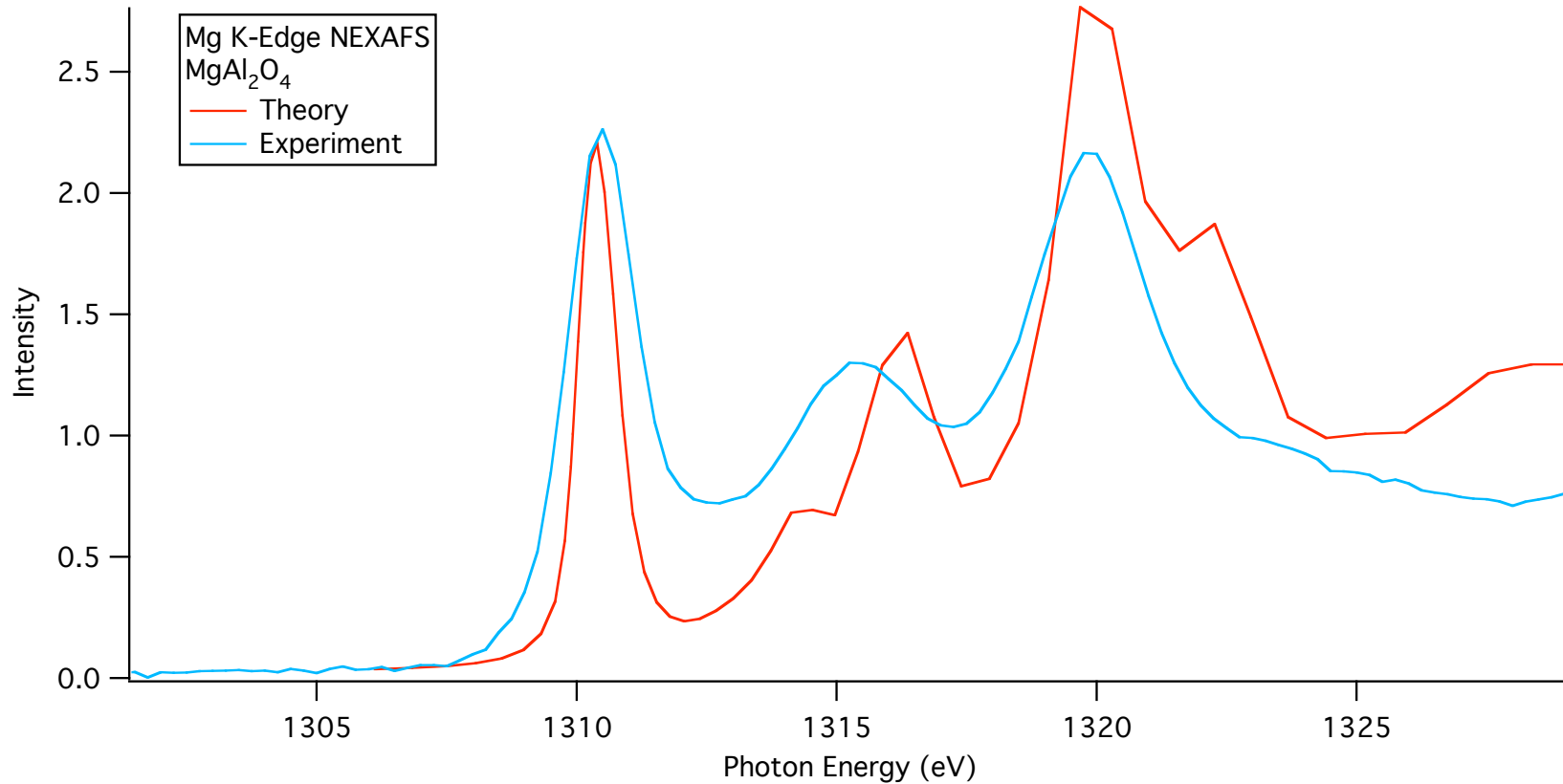


# RADIATION DAMAGE

## Mg K-edge NEXAFS



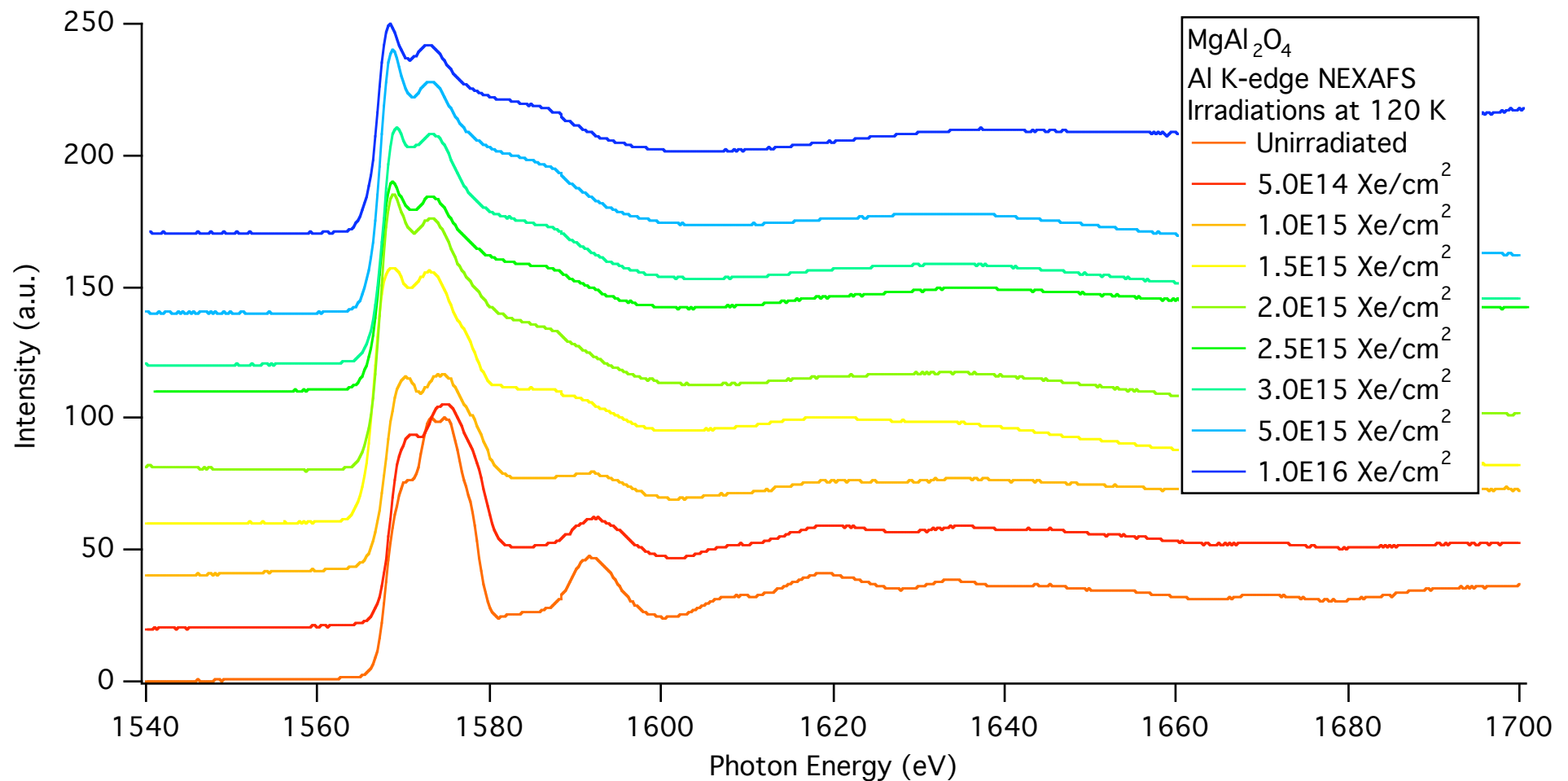
# RADIATION DAMAGE



• First Understand Starting Material

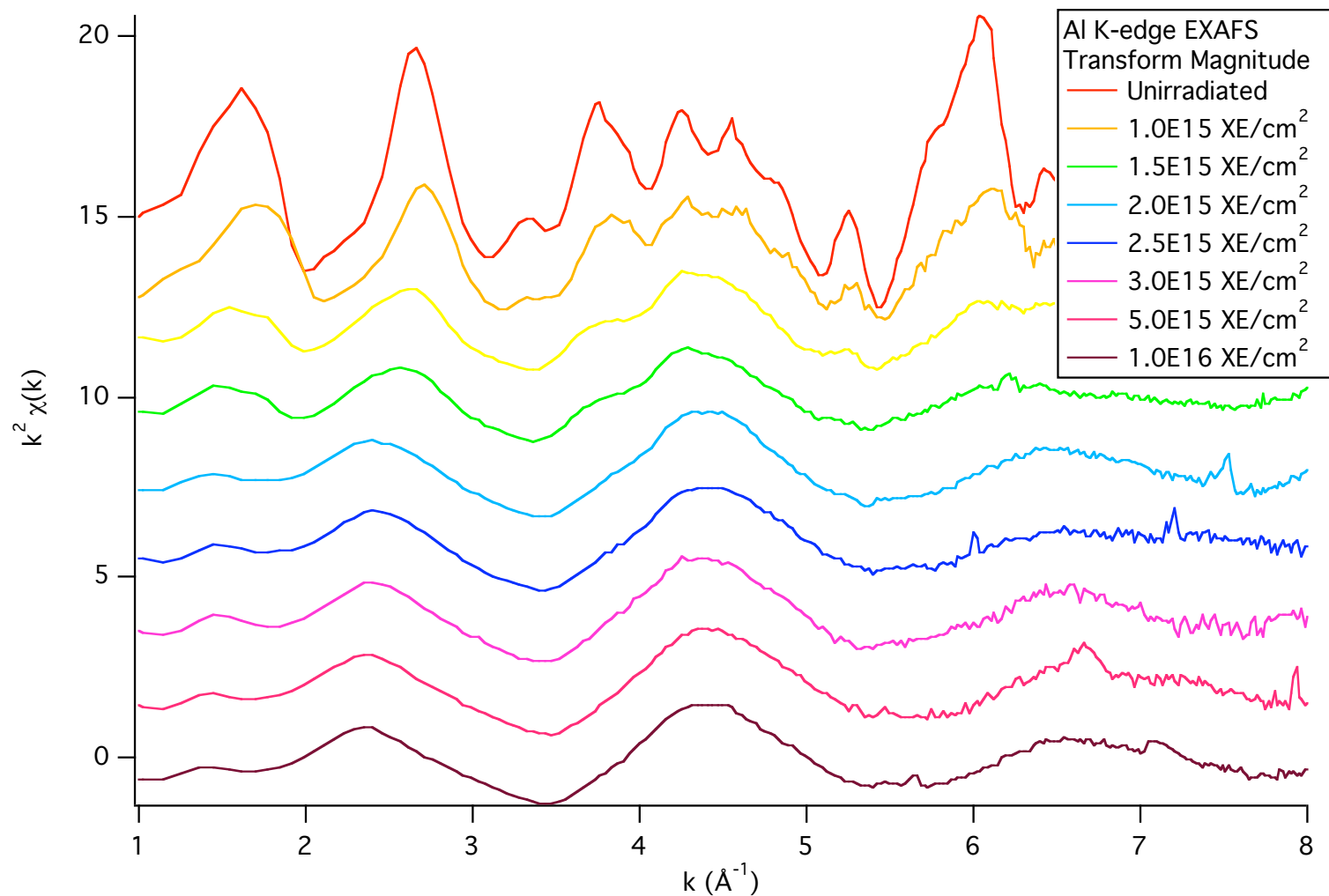
# RADIATION DAMAGE

Al K-edge XAS



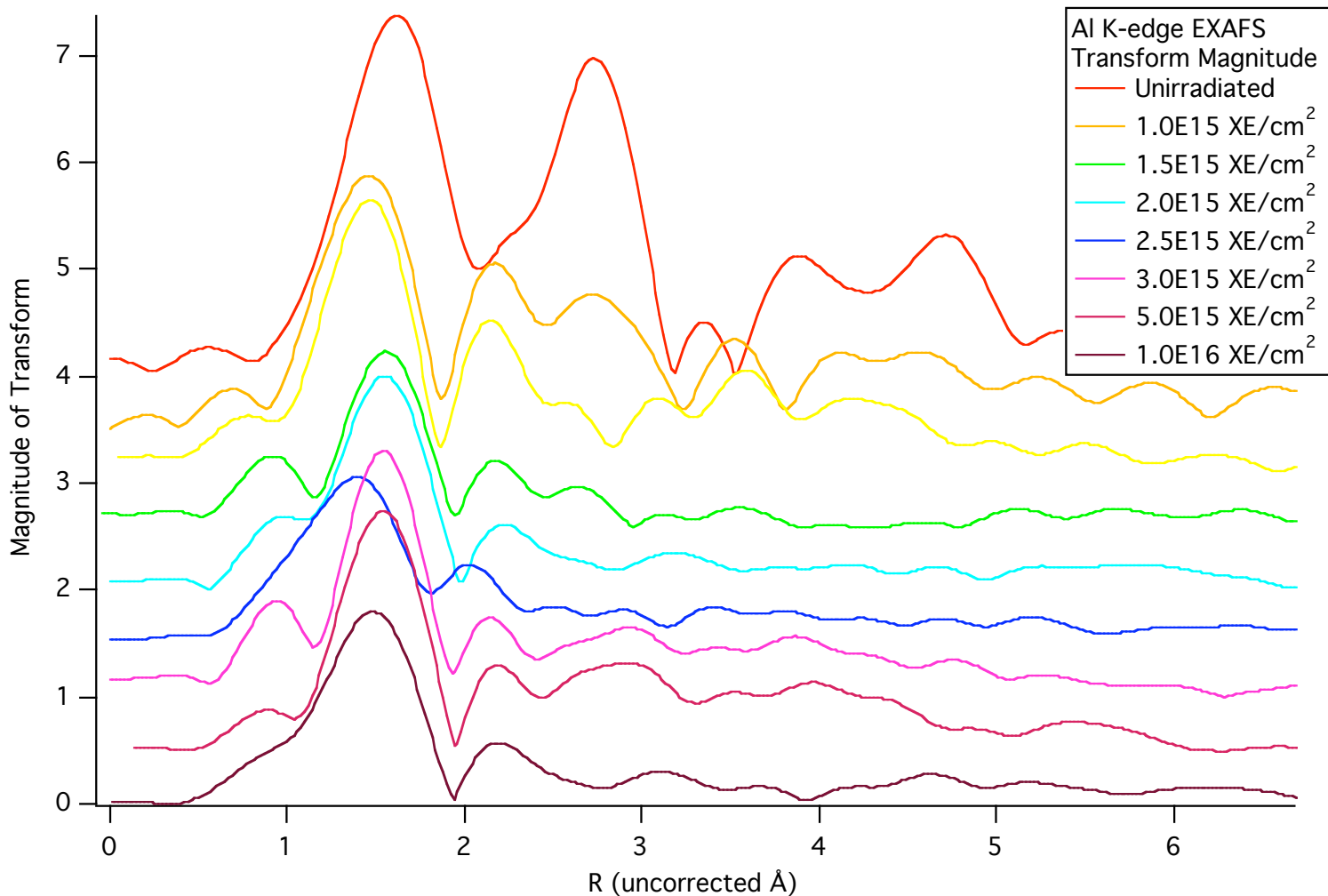
# RADIATION DAMAGE

## Al K-edge XAFS



# RADIATION DAMAGE

## Al K-edge XAFS



# RADIATION DAMAGE

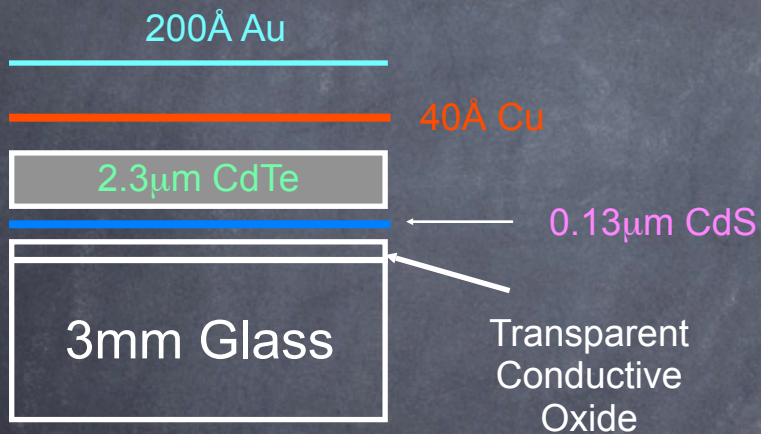
- X-ray Absorption Good Probe of Radiation Damage

# CdTe Solar Cells

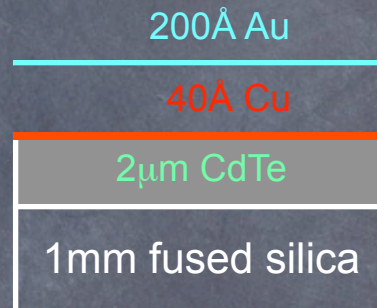
- There are some people that just don't favor Nuclear Power
- Try to understand the mechanisms that limit efficiency in Solar Cells

# CdTe Solar Cells

## CdTe based Cell



## EXAFS samples



Procedure:

2μm CdTe film on Qtz.



CdCl<sub>2</sub> treatment in **Air**



40~200Å Cu



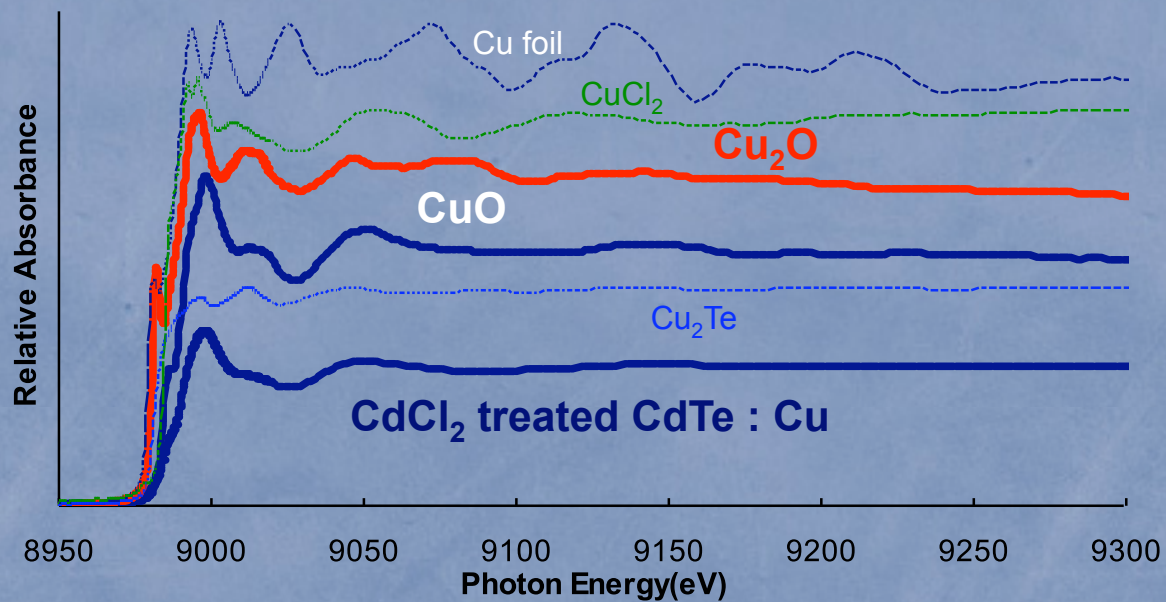
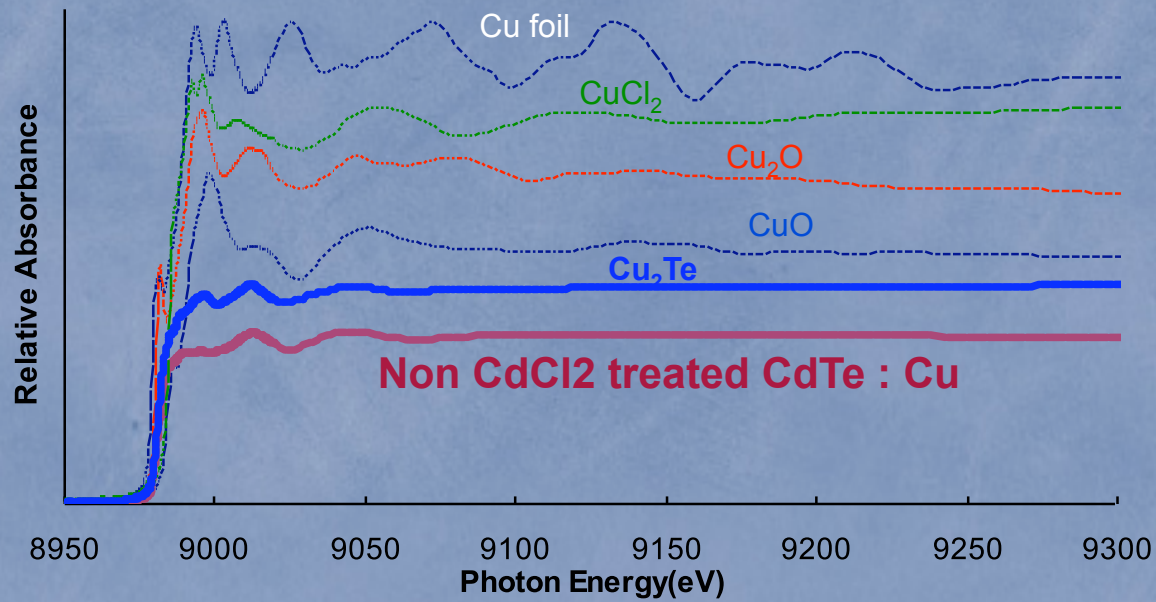
200°C Diffusion in N<sub>2</sub> for 45 min.



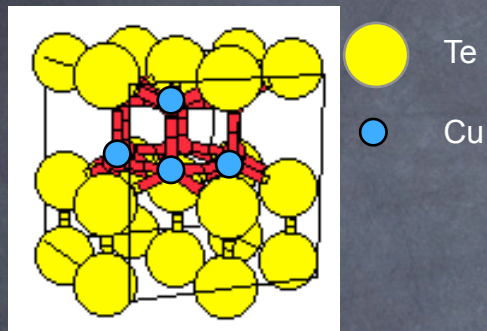
optional

HCl etching to remove elemental copper left on surface

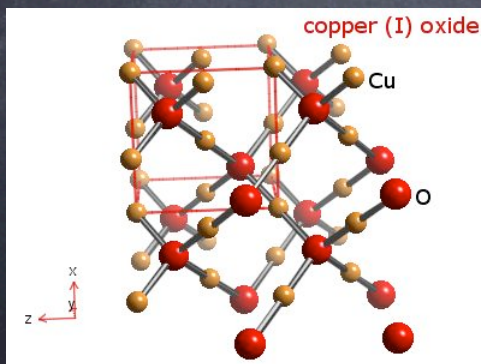
# XAFS



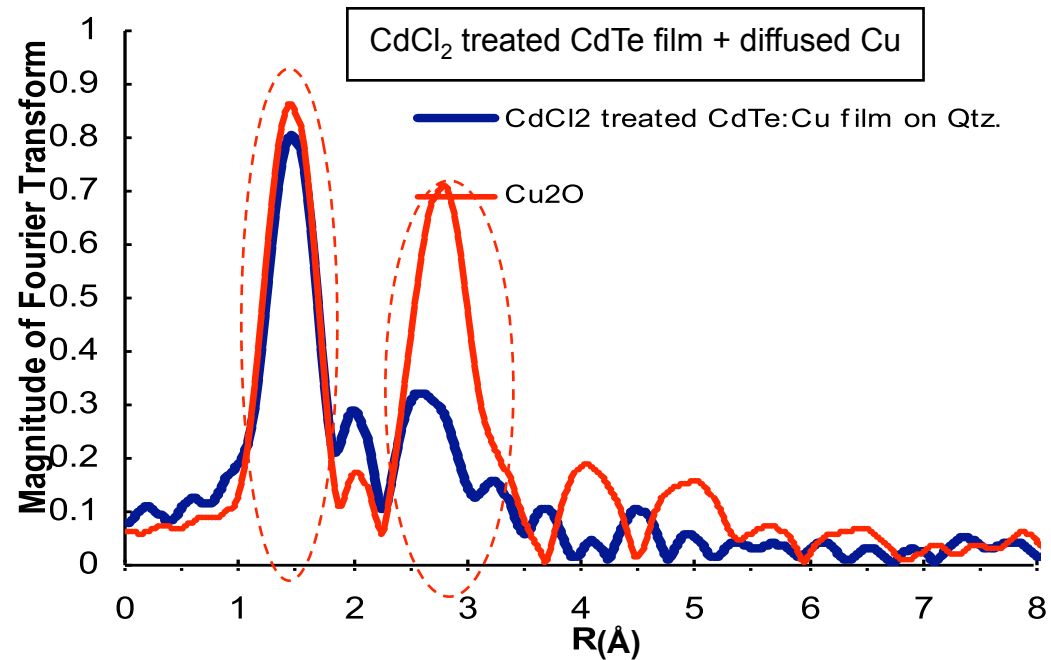
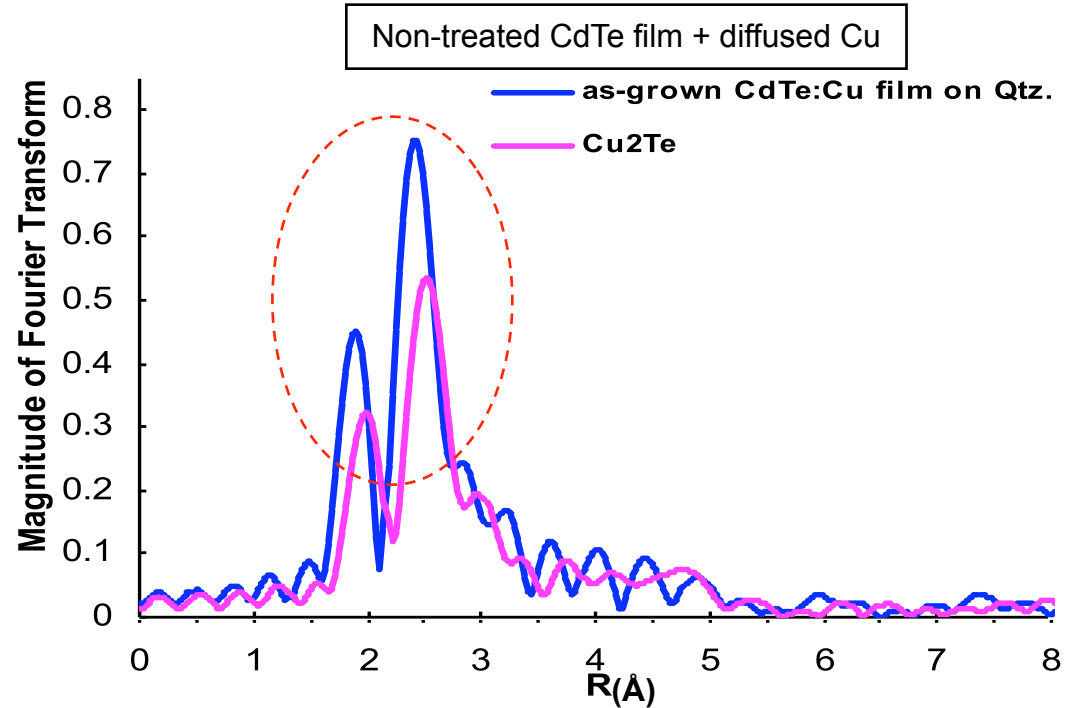
# XAFS



Cu<sub>2</sub>Te

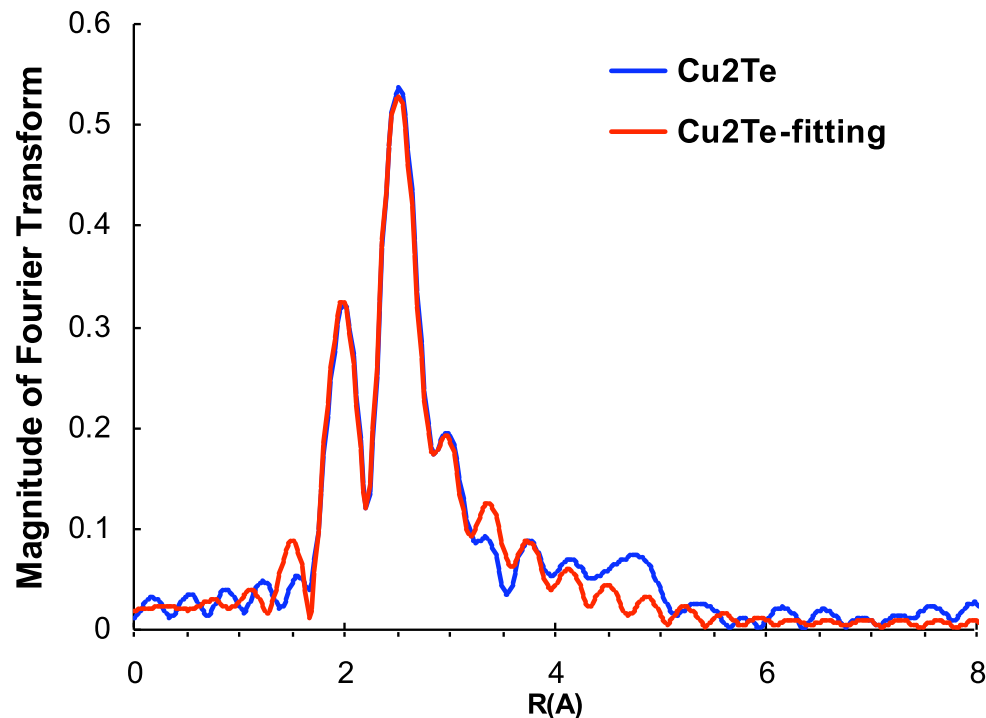
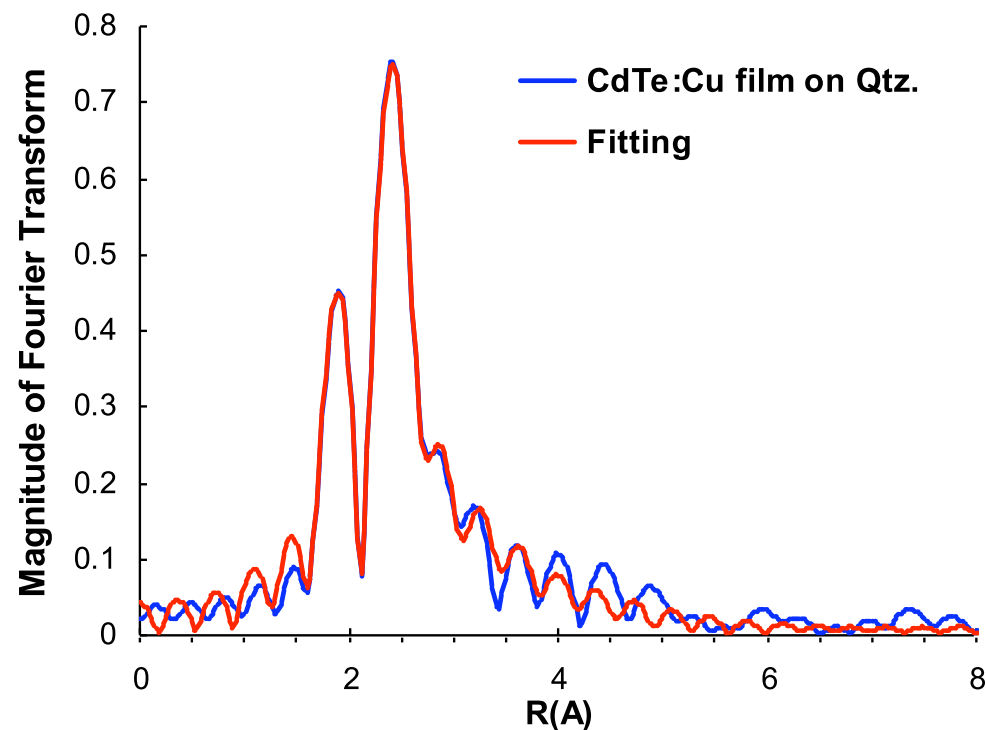


Cu<sub>2</sub>O



# XAFS

## FEFF theoretical fitting to $\chi(R)$



### As-grown CdTe:Cu film on Qtz.

bond scattering	N	dN(+/-)	R(Å)	$\sigma^2(\text{Å})$	$\Delta E_o$
Cu->Cu->Cu	1.53	0.39	2.22	0.010	3.69
Cu->Cu->Cu	1.45	0.37	2.45	0.005	
Cu->Te->Cu	3.78	0.96	2.56	0.024	

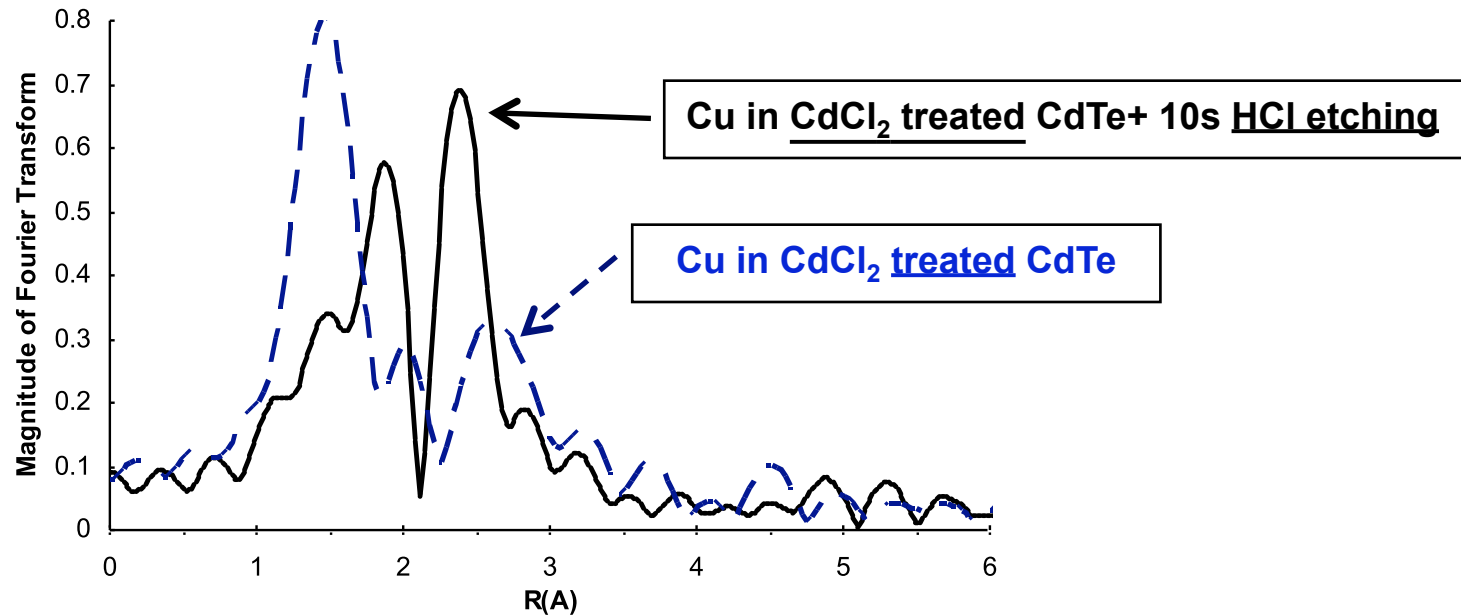
### Cu<sub>2</sub>Te

Cu->Cu->Cu	0.62	0.16	2.26	0.005	4.67
Cu->Cu->Cu	2.35	0.60	2.52	0.010	
Cu->Te->Cu	3.44	0.87	2.61	0.029	

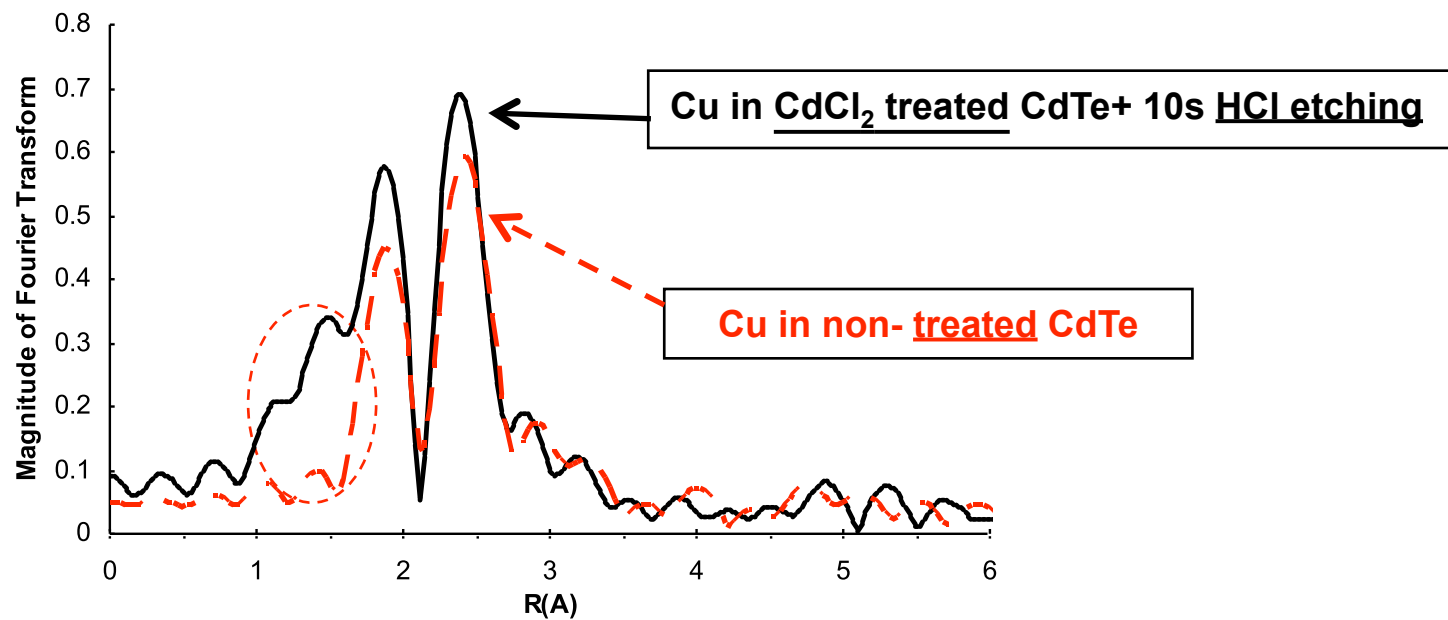
*Cu<sub>2-x</sub>Te forms in CdTe:Cu film*

# XAFS

Oxidized copper on Grain Boundary dissolved by HCl



Cu<sub>2</sub>O lost after  
HCl etching



# $\text{Cu}_2\text{O}$ $\text{Cu}_2\text{Te}$ $\text{CdTe}$

- $\text{Cu}_2\text{O}$

- Band Gap  $\sim 2.0$  eV

- $\text{Cu}_2\text{Te}$

- Band Gap  $\sim 1.5$  eV

- $\text{CdTe}$

- Band Gap  $\sim 1.5$  eV

- Band Gap Mismatch Inhibits Recombination At Grain Boundary

# Conclusions

- In polycrystalline CdTe film without Cl treatment, Cu resides predominantly in a  $\text{Cu}_2\text{Te}$  environment
- With Cl treatment, the chemical environment surrounding most of Cu atoms is similar to cuprous oxide  $\text{Cu}_2\text{O}$
- $\text{Cu}_2\text{O}$  resides mainly as mono-layers along the grain boundary
- $\text{Cu}_2\text{O}$  may play an important role in grain boundary passivation
- Hot off the press,  $\text{Cu}_2\text{O}$  forming clusters during light soak

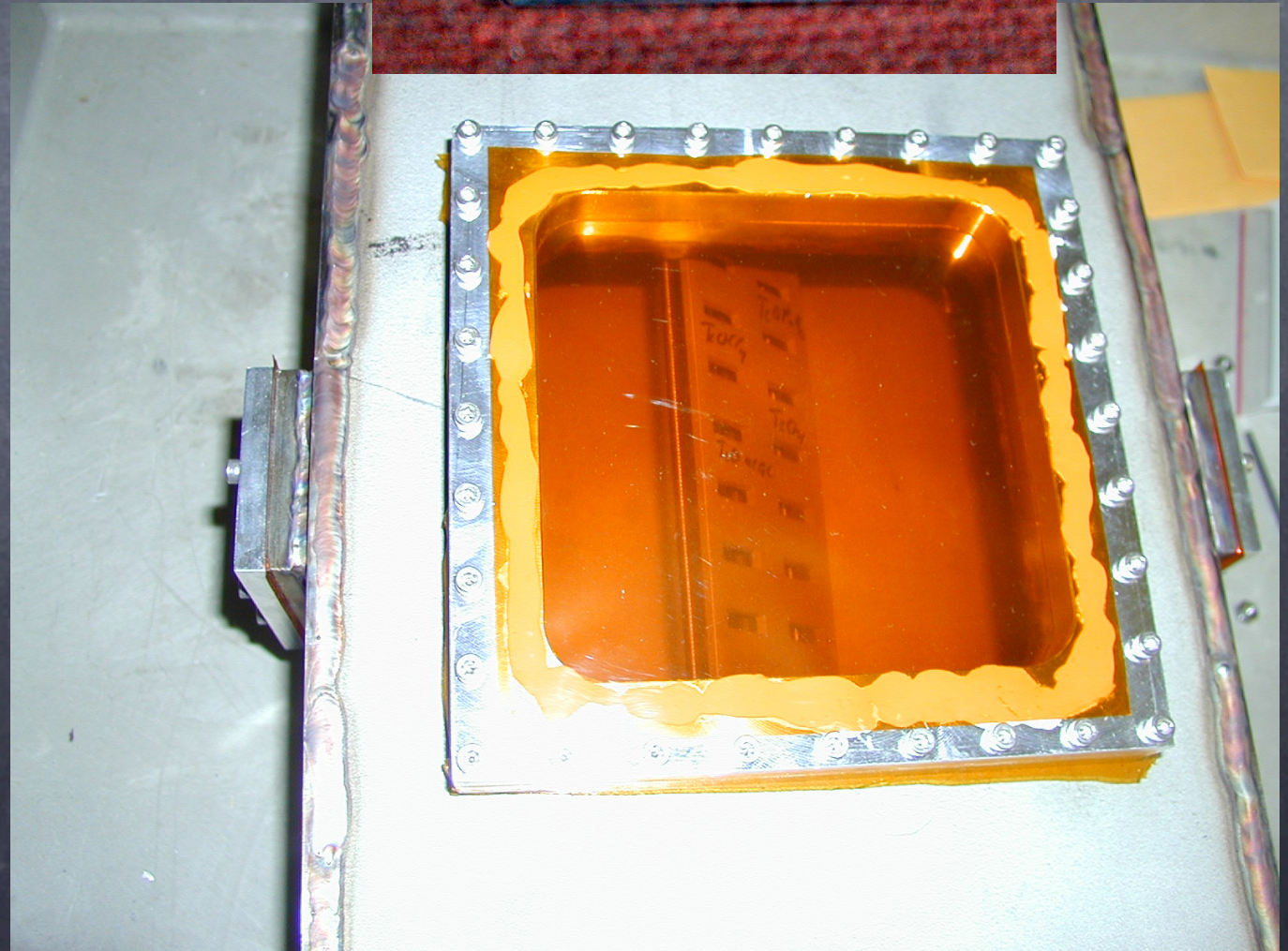
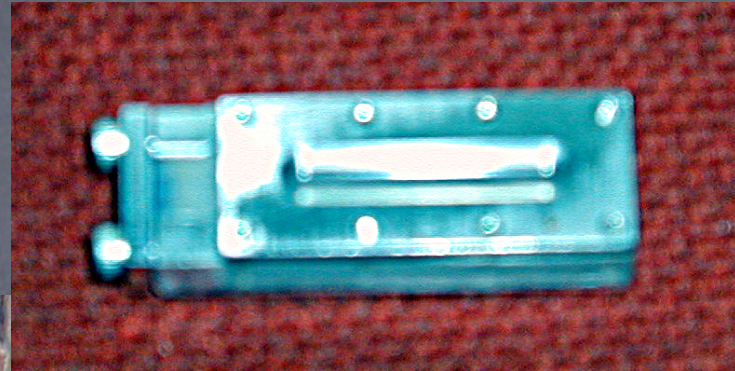
# ACKNOWLEDGEMENTS

- The Advanced Light Source is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.
- The Stanford Synchrotron Radiation Laboratory is supported by the Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences

# ACKNOWLEDGEMENTS

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- The Actinide Facility was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contracts W-31-109-Eng-38 and DE-AC03-76SF00098

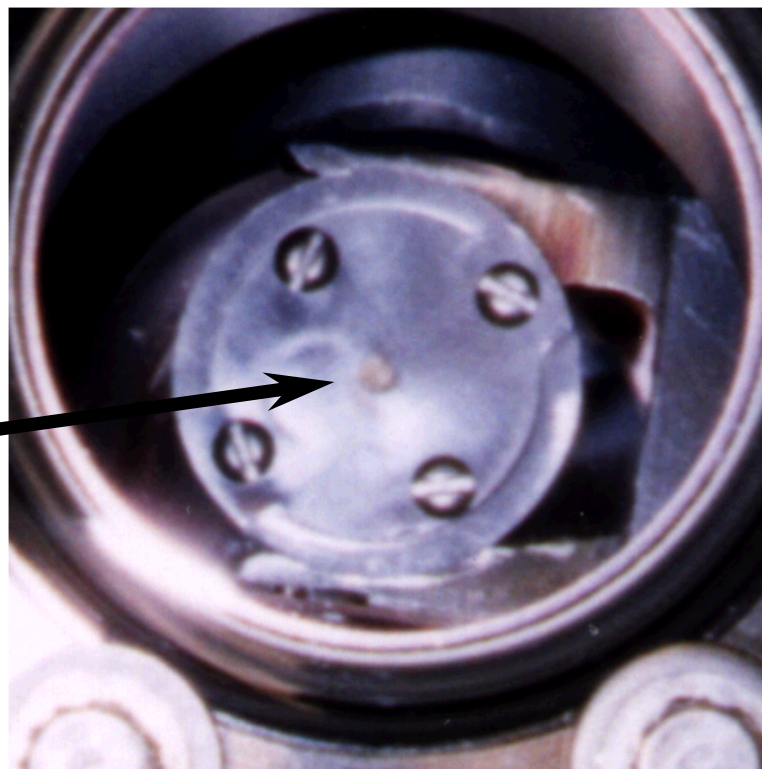
# XAS Experimental



- # Handling Radioactive Material

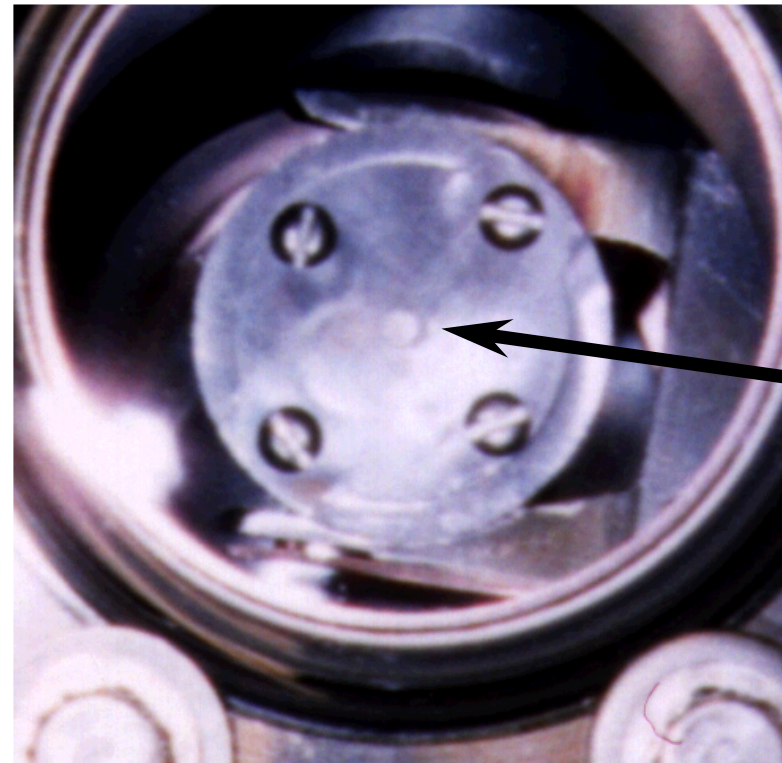
# Shipping Under Vacuum

- Battery Operated Ion Pump
  - Shipping Documents Pu - 1 page
  - Shipping Documents Excide Lead Acid Battery - 26 pages



Plutonium  
Disk

**Before Sputter**



Plutonium  
Disk

**After Sputter**

# Sealed Ar Container



# Measurement Cells

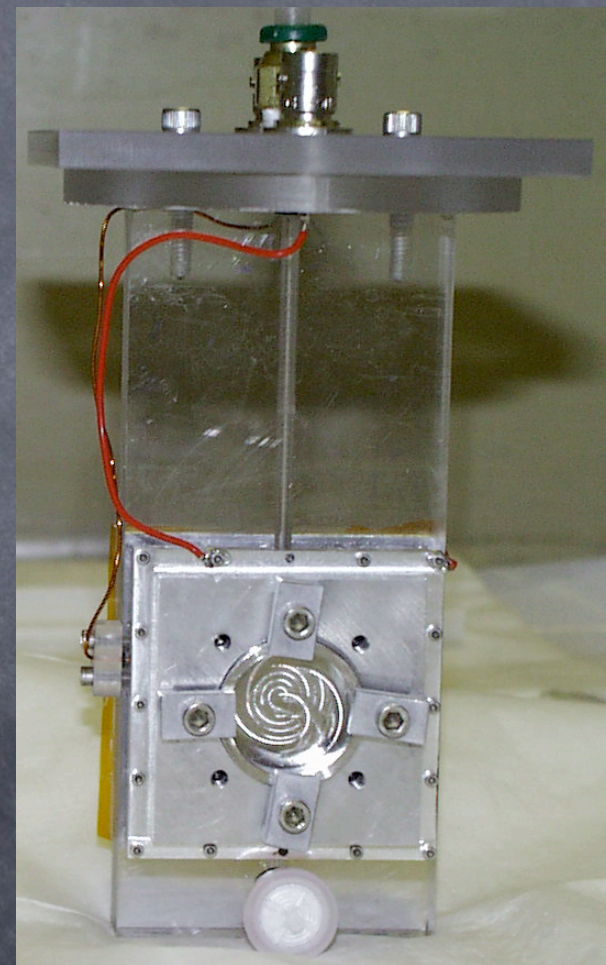
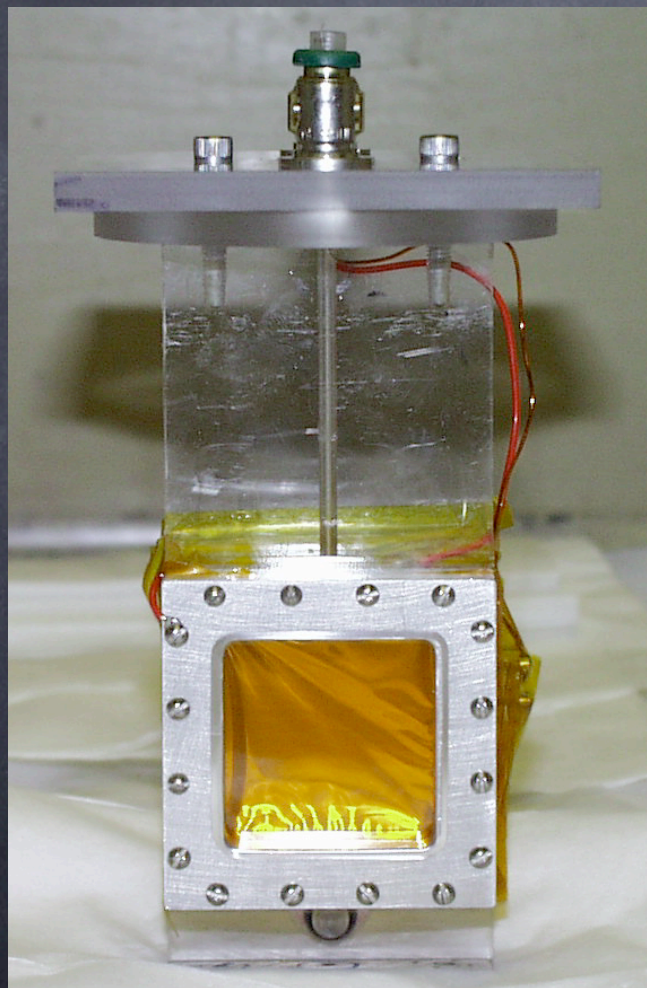
- Why E-Yield?

- Fluorescence-Yield Too

- Large Kapton Window Allows for Simultaneous F-Yield Measurement

- Details

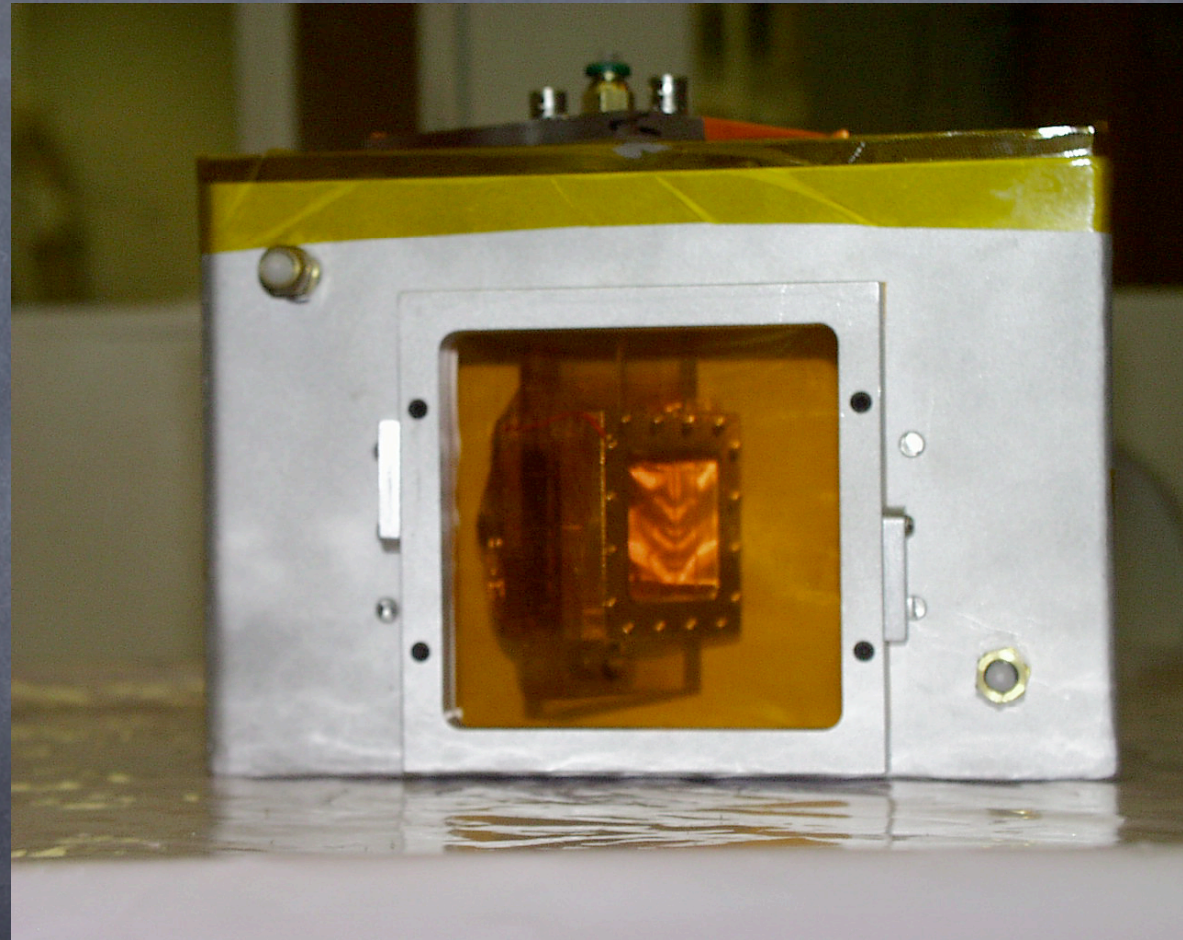
- Sample Sealed With Indium Wire and Multiple Kapton Layers
- System Filled With He for Electron Amplification
- Sample Biased -50 V



# BEAM LINE CONTAINMENT

- Kapton Sealed Container

- Three Large Windows
  - One Large Window In Front (Allows FY Light to Detector)
  - One on Each Side to Light Beam Into and Out of Cell
- Containment Vessel Holds Room Air



## LANL

- Repeated Sputter-Anneal Cycles to Remove Dissolved  $O_2$
- Samples Transferred to Vacuum Transfer Vessel

## Shipping

- Samples Shipped in Vacuum Transfer Vessel at  $10^{-8}$  Torr

## ALS

- Final Cleaning Done in Sample Handling and Integrated Transfer System for Pu Intense Light Experiments
  - Sputter 5 kV Ar ions
  - Anneal 75 °C

# SURFACE PREPARATION

